

of connection of the line into a manhole or adjacent catch basin. Figure 2 illustrates a typical dry box.

- Catch basins should be located so that the resulting pool of liquid, hydrocarbons or possibly a pool fire, does not expose adjacent areas. Some plants have been arranged so that pavement grading slopes to a low point underneath the pipeway which can result in an accumulation of hydrocarbons in the center of a unit under equipment and the main pipeway. If ignited the fire exposure to pipelines could result in opening additional lines, often in an explosive manner, loss of instrumentation and power lines which are generally run along the center of a pipeway. Since such areas are often congested and difficult areas to fight fires, the extent of fire damage to the unit could be catastrophic.

Sewage and Drain Ditches

The layout of the sewer system should be coordinated with the paving system to assure safe removal of spills and firefighting water. Spills from broken lines or opened equipment should flow to the sewer and should be away from high risk areas. Figure 3 depicts the typical arrangement and slab drainage in a conceptual process unit area.

Sizing - Sizing of an oily water sewer system depends upon the larger flow of either the rainwater (storm), demand, or the firewater demand. Major factors to consider include:

- Storm flow should be sized for the maximum credible flow, possibly the ten-year storm flow or higher if higher rates are commonly anticipated. In some areas this rate may be exceeded from time to time and plant operators should take special precautions under heavy storm conditions to assure containment of hydrocarbons in a containment pond or similar area.
- Maximum fire flow rate will depend on the type of process units with an average rate of 3,000-4,000 gallons per minute being the typical fire flow for a process area. In high pressure process units such as those with operations over 1,000 psig (hydrogenation, alkylation, or similar processes) firefighting flow rates can approach or even exceed 5,000 gpm. Where special uses of firewater have been installed, such as for HF Alkylation Units in refineries, flow rates of up to 20,000 gpm have been proposed for installation in existing plants. Such units will require extensive drainage provisions to prevent extensive accumulations of water in the process unit.
- Oily water or storm sewers that do not use gravity flow but

depend on lift pumps require special consideration of flow rates for storm conditions. Sewers often contain some residual oil which, if the lift pumps fail, will back out of the sewer through inlets or manholes and result in extensive spread of oil over large areas of a plant.

Catch basins are typically sized for 500-750 gpm each. Drainage system sizing is cumulative between catch basins, however, is often overlooked in basic system design or in plant expansions. The design should include a safety factor by sizing drainage piping to less than full capacity so as to allow for expansion of the process unit, accumulation of debris within the piping and simultaneously firefighting and storm demands.

Manholes - Inlets to manholes should be fire sealed to minimize fire spread within the fire system. Often the design includes the following additional considerations:

- Manholes should be vented to relieve excess pressure caused by vaporization of light hydrocarbons in the system. This is depicted on Figure 4 which shows a sealed, vented manhole in a concrete or clay pipe system and multiple inlets.
- Solid covers should be used to prevent vapor release and entry of sparks or other ignition sources.
- To control vapor release, combination manholes and catch basins should be avoided.
- Vents for manholes should terminate 20 feet or more above grade at a safe location. In order to satisfy environmental concerns over fugitive emissions, pressure-vacuum vent devices with a flame arrestor are often fitted on the vents to prevent fire entry.

Fire Seals - Fire seals should be installed in sewer lines serving more than one unit at the connection with the unit and on 500 foot intervals in main sewer lines. Fire seals will prevent flame promulgation and possible explosions in the main sewers and connecting unit sewer lines.

Open Ditches - Open ditches should be avoided whenever possible due to the potential for fire spread unchecked between large areas of a plant through the open ditch system. The use is however required where hydrocarbon materials such as spilled LNG and often LPG could potentially form ice plugs when vaporizing, freezing of the liquids in the sewer and damage that results when pressurizing the drain piping system. Thus open trenches are commonly used for refrigerated and liquified gas processing units. Under such conditions the slope of paving should accentuate towards the direction of drainage so that spills flow rapidly away from equipment and provide minimum exposure to

liquids in the drain trench which can result in excessive vaporization of spills.

Drain Ditches - Drain ditches should be located away from equipment in a process unit. When locating drain ditches the following precautions should be observed:

- Provide fire seals at natural barriers such as at road crossings. Fire seals should consist of a clear space of 50 feet between exposed portions of the open trench. This can be provided by use of a fire seal constructed of culvert pipe extended from each side of a road crossing the trench.
- An inverted weir or pit with a downward elbow should be installed on the inlet end of the fire seal. Seals should be spaced at an interval which provides for control of fire in the ditch and minimizes exposure to adjacent areas. Often these seals are spaced at a distance of 500-1,000 feet apart.
- Pipeways that cross ditches should be protected from fire exposure. This can be provided by providing a hydrocarbon fire rated fireproofing on the piping or by installation of manually actuated water spray system to cool the pipelines to prevent fire damage.
- Drainage ditches should be arranged to protect pumps or equipment located adjacent to ditches. Protection can consist of ditch covers, fire water monitors or water spray manifolds. Where pump pads can not be properly segregated from drain ditches fixed water sprays, water monitors and other equipment should be provided to ensure safety of the operating equipment. A typical plant may have pump pad manifolds immediately exposed to a fire in a drainage ditch. Pump manifolds not protected by fixed protection should be located in paved areas with accentuated slope to adjacent drain areas which are well separated by fire sealed piping.

Containment Areas

Increased emphasis on the environmentally safe collection of storm water and discharges from oily water sewers to prevent contamination of adjacent waterways, has created new fire safety challenges. Containment basins should have the following features:

- The basin or area should be located downwind of process units and service areas so as to minimize the potential for personnel exposure to vapors and possible ignition. Remote location of these basins is an accepted design practice, however, potential exposure to the public nor to standing ignition sources such as flares or roadways should not be

overlooked .

- Separation of catchment basins from property lines should be considered so as to prevent possible vapor cloud and/or fire exposure to or from surrounding properties. Natural growth fires should not be overlooked as an exposure to large potential accumulation of hydrocarbon and vapor emissions from such areas.
- Containment basins should be liquid tight and constructed of impermeable materials that will prevent soil and ground water contamination. In some areas it may be necessary to provide secondary containment for the containment basin. In other locations concrete basins or other kinds of surface preparation including membrane or sprayed coating materials may be necessary to assure safety for the environment.

TANK FARM AND STORAGE DRAINAGE

Safe arrangement of drainage in a tank farm must consider a number of interrelated elements. The slope and arrangement of the dike area adjacent to the tank is a critical factor in assuring that small spills, if ignited, do not expose the tank to a fire. The dike should be properly arranged to contain spills or the full release of tank contents. In addition, water and spills should be safely conveyed from the dike area to waste water treating or storm treatment areas. A further factor in tank farm drainage safety is the arrangement of the pipeway which should be properly configured to prevent spread of spills from tank dikes into the pipeway or vice versa.

Dike Area Drainage

Safe arrangement of dike areas is detailed in National Fire Protection Association (NFPA) Standard No. 30 - *Flammable and Combustible Liquid Code*. The basic objective of NFPA 30 requirements is to prevent any discharge of flammable or combustible liquids from endangering important facilities, adjoining property, or reaching waterways. NFPA 30 contains an exception to diking requirements for Class IIIB liquids combustible for drainage or diking provisions. Although this exclusion will apply for fire protection purposes, it is likely that environmental concerns will impose diking and containment requirements.

Dike Construction and Arrangement

Dikes are used to control or contain a spill or firefighting water and are used typically in storage tank areas. The most preferred method of diking is remote impounding since this arrangement removes the spills, storm drainage and firefighting water to an area remote from the tanks minimizing potential for exposure of the tanks to fire effects. Where remote impounding

is not feasible, due to location or cost, containment dikes are typically used.

Remote Impounding - Remote impounding is the most desirable method for containment of spills from flammable and combustible liquid tankage. The remote impounding arrangement is such that spills are carried away by sloped ground to an impounding basin which is located so that there is minimum exposure to adjacent facilities and equipment. This arrangement is much more preferable since no liquids remain around or under the equipment. Remote impounding however generally requires large available spaces and thus may be economically impractical.

Impounding basins should be maintained dry and empty and if full of water adequate freeboard should be provided for the largest spill that may be diverted to the impounding basin. To the degree practical, the surface area of the retention basin should be maintained at a minimum size which will reduce the vaporization of spilled liquids. Foam can be applied on spills to reduce formation of vapors however application on a large area may not be feasible due to limitations on water supply or foam generating capacity or due to other features of the area.

A remote impounding basin is typically sized to handle the contents of the largest tank connected to the basin, assuming the tank is full, or the largest liquid volume that can not be readily isolated plus fire protection water. Various jurisdictions differ, however the minimum size should be 100% of the largest tank expected to divert a spill to the basin.

Containment Dikes - Dikes which impound spills in an area adjacent to and around the tanks are the most common type of diked enclosure. Various jurisdictions will differ on the sizing of the diked but at least the area should be sized for 100% of the contents of the largest tank within the enclosure. The volume of the smaller tanks within the diked area up to the height of the dike must be considered in calculating the dike capacity and this volume added to the dike area since it is not available for containing liquid spills. The Flammable Liquids Code Handbook published by the NFPA contains various examples on calculation of the volume of a diked area. When diked areas contain two or more tanks the diked area should be subdivided, preferably by drainage channels or by intermediate dikes to prevent spills from spreading from the area of one tank to an adjacent tank. Spill dikes should be designed to contain approximately 10% of the largest tank volume within the spill dike area. Low 1-1/2 to 3 foot high spill dikes will prevent any small spill from exposing other tanks or equipment within a diked area. Spill dikes or subdivision dikes are less in height than main containment dike heights. They also can be used to control a liquid spill from pressurized storage tanks, however placement of pressurized storage in the same dike is not normally

considered good practice.

Dike Walls - Dike walls can be made of compacted earth, concrete or solid masonry and should be designed to be liquid tight. Penetrations through the dike wall should be designed to withstand full hydrostatic head of the impounded spill. Where concrete dikes are used, expansion joints and sleeves with full packing for piping penetrating the wall is required to prevent liquid flow outside the dike wall. Masonry walls are not likely to survive for any appreciable time when exposed to a major tank fire and thus are not as acceptable as a dike wall constructed of concrete. Masonry walls can be heavily reinforced against thermal and hydraulic stresses. Dikes should also be designed to withstand fire, earthquake, wind and rainfall exposure.

Special provisions are outlined in NFPA 30 for dikes of higher than six foot. Where these provisions are not in place, the average height of a dike should not exceed six feet to allow easy firefighting access. This height also provides better natural ventilation and dilution of any vapor accumulation. High walls that are close to flammable storage tanks should not be used in place of dikes since this impairs firefighting access and provides a major fire exposure to the tank. NFPA 30 contains special provisions for high dike walls which increase safety where such provisions are absolutely required due to site conditions.

Vehicle access ramps into diked areas are not desirable, however operations may require that they be provided. Operators should be restricted from entering diked areas without entry permits which include gas tests similar to that used for hot work. Access roads and tank farms on top of dikes may be provided in older tank diked areas, however multiple roads to access all areas of the tank farm will be necessary since under some conditions fire could block the use of roads on top of the dikes. Care should be taken in design of diked areas with roads on top of the dike to insure that heavy traffic does not damage or settle the dike.

Piping In Diked Areas - Where piping is provided in diked areas it should be a minimal amount. When exposed to ground level spill fires, pipes usually fail within 10-15 minutes of initial exposure releasing contents and spreading fire. Quick couplings, cast iron fittings, or compression style fittings are all susceptible to fire exposure and can easily fail and spread the fire by releasing piping contents. If possible, pipes should be buried or located above a berm to prevent burning liquids from pooling under the piping. Piping should be run to pipeways outside the dike wall to prevent extending pipelines through dike walls between adjacent diked areas.

Diked Area Drainage - It is not necessary in all cases to provide

safe location. Operational considerations have a large impact on the arrangement of grading and paving spill collection systems and the specific requirements for preventing spills from traveling between adjacent building areas. Multi-floor process facilities present unusual design requirements to prevent inter-floor passage of spilled hydrocarbon materials and fire protection system water. Measures are also needed to assure that spills are directed to a safe containment system instead of into exit passageways or other areas where spills would result in serious fire and safety concerns.

Specific requirements for arrangement of interior process areas containing flammable and/or combustible liquids are contained in NFPA 30. In addition, the model building codes contain specific requirements for hazardous facilities. In general, these provisions require consideration of the following factors:

- Emergency drainage should be provided to direct flammable or combustible liquid leakage and fire protection water to a safe location.
- A drainage system is a combination of curbs, scuppers or special drainage piping systems which control the spread of fire through the facility.
- Drainage systems connected to public sewers or where discharged into public waterways should be equipped with traps, separators or other means to prevent travel of hydrocarbons off the facility.
- Normal discharge of flammable and combustible liquids into public waterways, sewers or adjoining property should be prohibited.

Inter-floor Protection - The greatest exposure to interior process units is the potential for spills to travel through more than one floor of a facility. Travel can occur through openings around pipes and equipment, process facilities and vessels. Where equipment, piping or vessels penetrate solid floors, the opening should be provided with a curb or a sleeve to prevent spills from traveling through the opening to a lower floor. Curbs, ramps or other similar means of preventing passage through the openings in the floor should be provided.

Grading and Paving of Floor Surfaces - In a similar approach as for exterior process units, enclosed process area floor slope should be accentuated to hubs, drains or trenches designed to convey spills and fire protection water away from equipment and areas of operator egress. Floor inlet drains should be provided with traps or seals to prevent passage of vapor between floor areas. Some operators have instituted use of automatic filling of flame traps with water or water-glycol mixes to provide proper

fire sealing in the interior floor drain system. Inlets should be generously sized to handle fire protection water for the largest water flow anticipated on that floor or area of the building. Modern fire protection systems are sized to provide large volumes of water into areas of process buildings where flammable or combustible liquids are handled. Due to the quantities of water released from the fire protection system, generous drainage system size should be anticipated in the original design.

Trenches, Curbs, and Ramps - Trench drains similar to those specified in Appendix A of NFPA 15 - *Water Spray Systems*, should be used to prevent spread of open fire in trenches. Where necessary, limited use of trenches can be made of trenches placed at fire doors, exit doors or to segregate storage areas of different commodities. Floor trenches have the disadvantage of being susceptible to accumulation of debris which will plug the drain. Ramps are used to provide passage through fire door openings or similar areas, such as indoor storage areas for flammable liquid containers. The ramp should be arranged so that it is not a hazard to the use of industrial trucks and result in the loss of a load. In general, NFPA 30 requires that noncombustible liquid tight trays, sills or ramps at least four inches in height be provided and designed to prevent the flow of liquids to adjacent areas. In some cases review of the design of the enclosing wall up to the four inch height will be necessary to assure that a spill within a room or area does not move around the doorway ramp or sill into adjacent areas through a wall which is less than liquid tight.

Drainage Piping Systems - Piping should be fire resistant steel or cast iron construction. Plastic piping systems should not be used to convey flammable liquid spills and fire protection water to the drainage system. In general, the provisions of NFPA 30 relating to piping system design will also apply to drainage system piping. Piping for underground sewers and connections to the oily water sewer or waste water treating area should be arranged similar to that in an outdoor or open air process unit. In general the piping should be rated for exposure to the hydrocarbons or chemicals that will be in the piping system and should be suitable for use in underground drainage systems. Manholes and inlets in the system piping should also be arranged with fire seals as previously discussed for open air facilities.

Building Spill Containment - There has been an increase in public and industry attention to the environmental concerns associated with the release of flammable or combustible liquids within a building. Buildings should have properly arranged hydrocarbon or chemical sewer systems. Building codes contain requirements for minimum safe design for systems handling hydrocarbon or flammable liquid removal. As a result designers are attempting to provide measures to contain hydrocarbon spills with firefighting water on

the property of facilities containing hazardous materials. While these provisions differ, generally they are consistent with the provisions of NFPA 30 discussed previously for closed process buildings. Because of the unique nature of many of the facilities requiring this protection method some unusual patterns have emerged in recent designs. In some cases owners are sloping warehouse and storage facility floors to outside walls where special containment areas are constructed, sometimes including areas of parking lots or loading docks. Since water flow rates in many facilities can be rather large, requirements for one or two hour runoff containment requires extensive areas for containment and impounding. A more desirable arrangement is to provide drainage systems within the building or to subdivide the building so that spills in one area do not travel through the entire facility before exiting to the impound basin. Often in hazard waste facilities, catch basins, inlets, or piping systems below the floor require extensive double containment to assure protection of the environment. These facilities require special engineering judgment and care to ensure that spills do not travel through the entire facility and increase the hazard instead of containing the hazard to smaller, more manageable areas.

SUMMARY AND CONCLUSION

The provision of adequate drainage in a safe manner is a key factor in flammable and combustible liquid handling facility design. Process plants, chemical facilities, and storage and handling areas all require special engineering attention to reduce the hazard of uncontrolled drainage. Existing facilities will require consideration of those provisions for new plants and, where possible, rearrangement or new facilities provided to assure safety in the facility. It is imperative that Process Hazard Analysis (PHA) reviews include a detailed examination of the drainage system and plant systems for drainage and water removal to assure safety of the plant during fire exposure conditions.

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Drain.Doc

ATTACHMENTS

FIGURES 1, 2, 3, AND 4

FIGURE 1

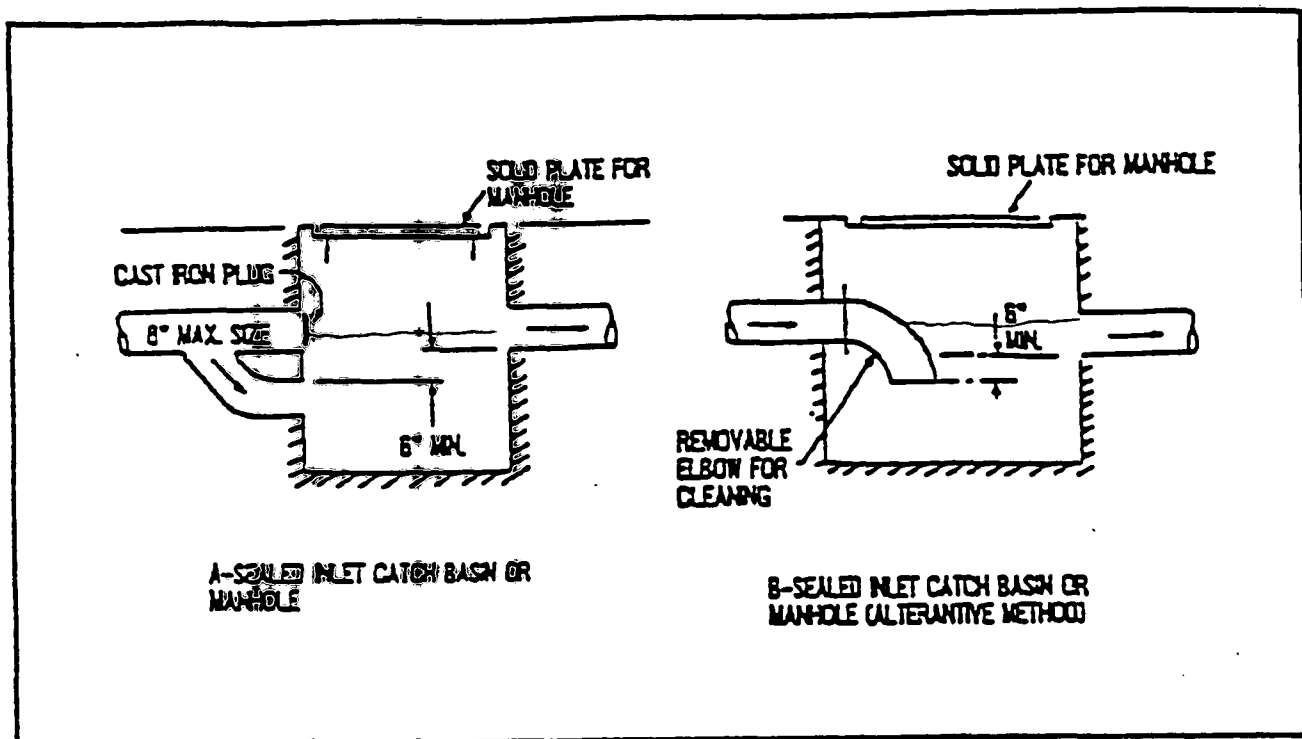


FIGURE 2

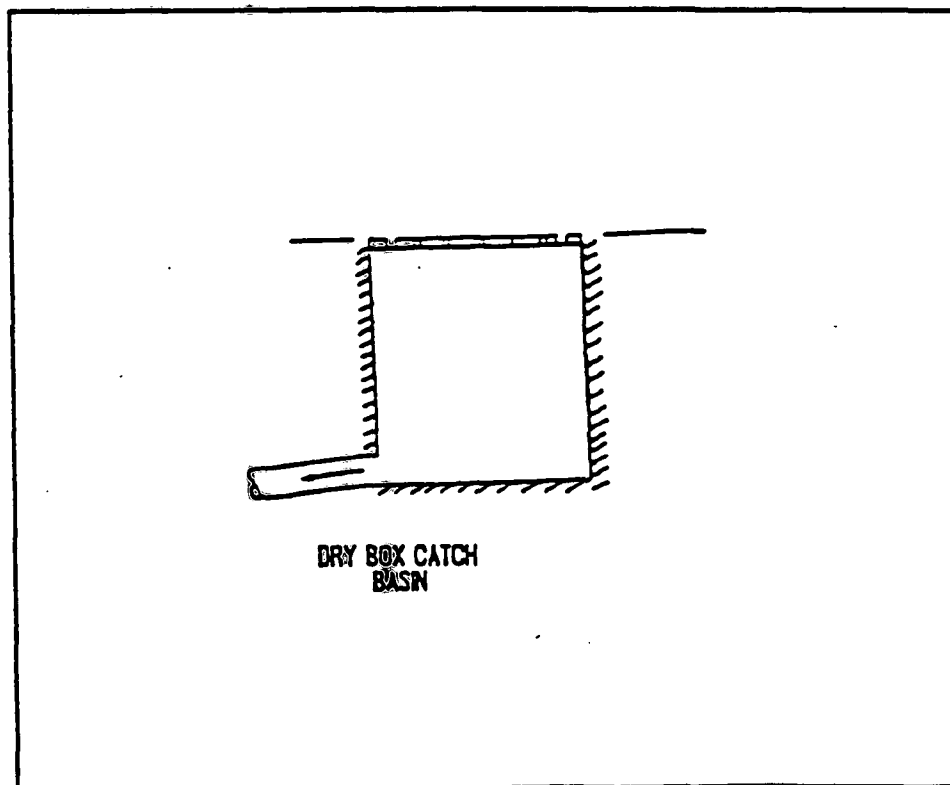


FIGURE 3

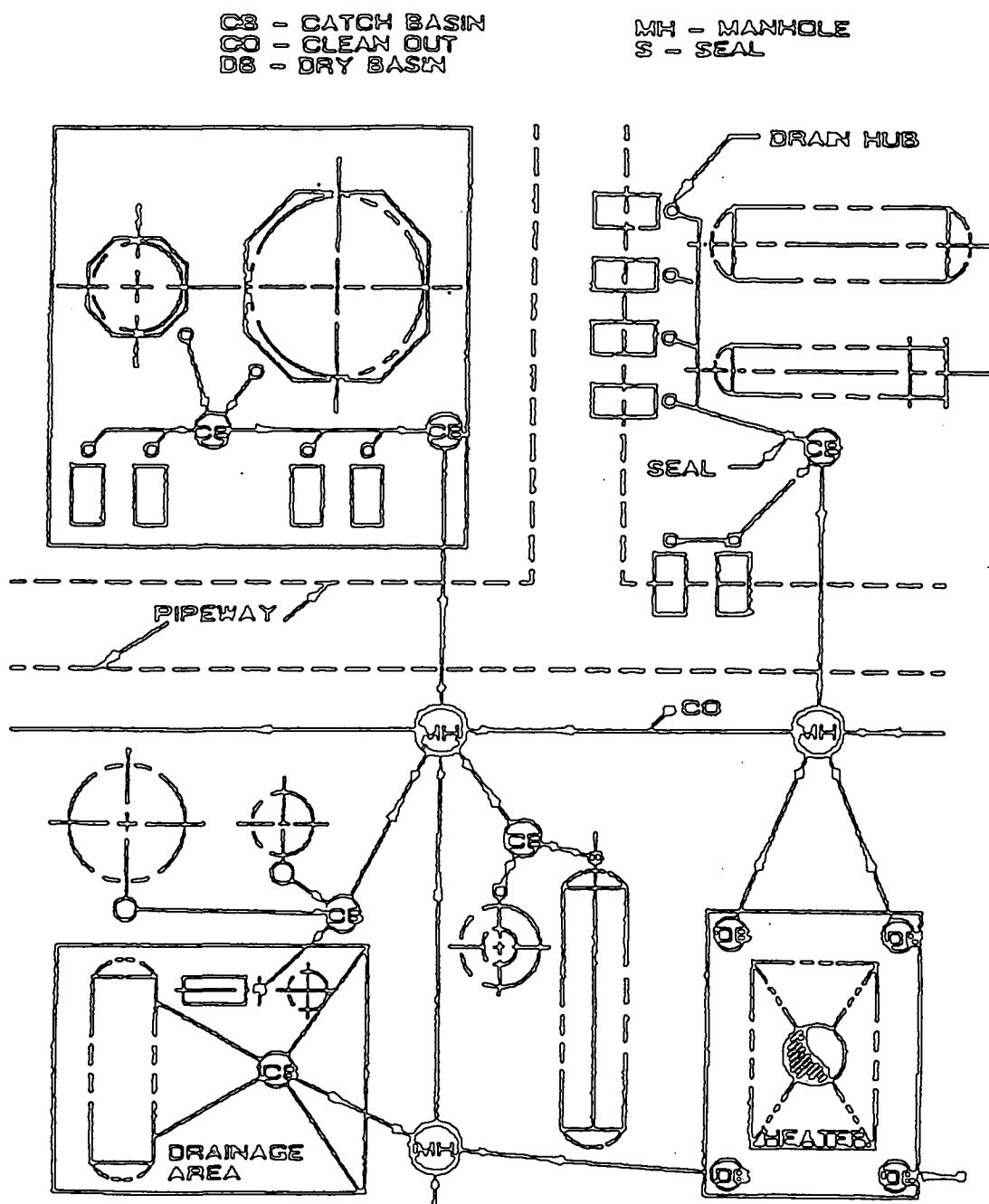
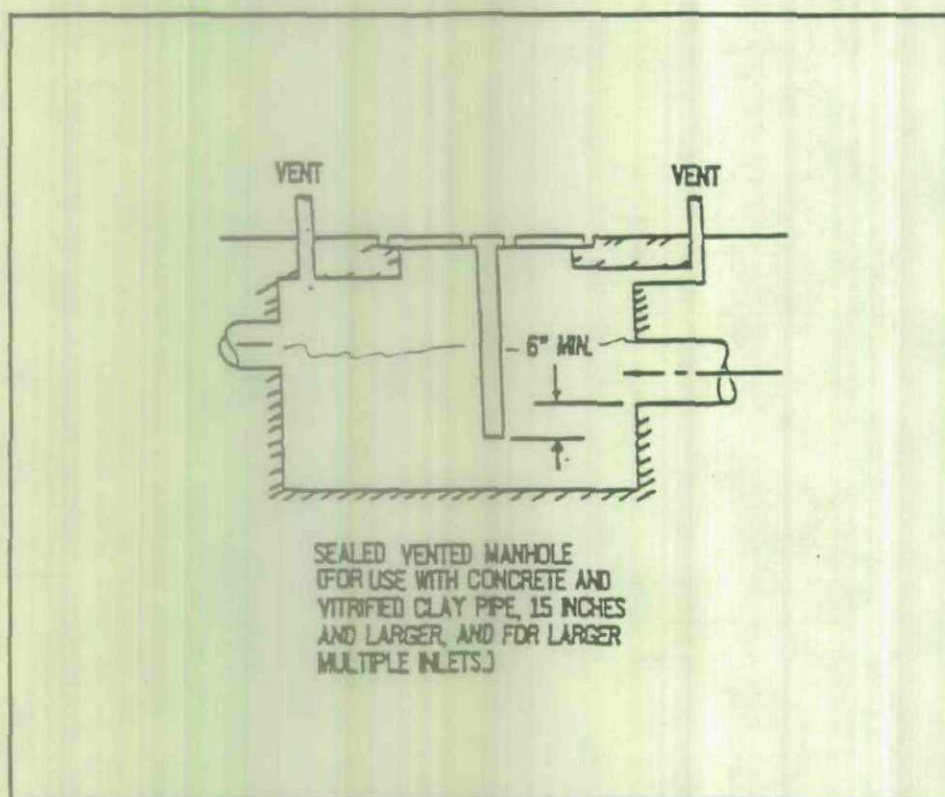
TYPICAL EQUIPMENT AND SLAB DRAINAGE
ARRANGEMENT

FIGURE 4



APPENDIX P

APPENDIX P

**Measurement of Hazardous Air Pollutant Emissions From
Wastewater Collection System Components**

Volume I: Drop Structures
Volume II: Process Drains

Submitted to:

**E.I. du Pont de Nemours & Company
Engineering Department
Wilmington, Delaware**

by:

**Enviromega Ltd.
P.O. Box 1249
Burlington, Ontario
L7R 4L8**

in cooperation with

**University of Guelph School of Engineering
Wastewater Technology Centre**

April 7, 1993

ENVIRΩMEGA

EXECUTIVE SUMMARY

In September 1992, Enviromega, in cooperation with the Wastewater Technology Centre and the University of Guelph School of Engineering, commenced an experimental investigation of fugitive hazardous air pollutant (HAP) emissions from drop structures and process drains. Pilot scale structures were constructed to simulate full scale operating conditions. Tap water, dosed with representative HAPs, was used as process wastewater. Both wastewater and off-gas samples were analyzed for the dosed HAPs, allowing for a direct measurement of emission rates. The emission rates measured during these studies are site specific and should be applied with prudence, especially given the potential complexity of individual collection systems. Simple emission factors should not be derived. Mass transfer coefficients measured during these studies can be used to calibrate models for predicting HAP emissions from wastewater collection systems.

Measurement of HAP Emissions From Drop Structures:

Eight experiments were completed to study HAP emissions at sewer drop structures. Five VOCs and methanol were used as representative compounds. Water flowrate was held constant at 6.8 m³/hr for each experiment. Three experiments were completed with a drop height of 1.0 m, with sequentially increasing headspace ventilation rates. Five experiments were completed with either partially or fully-submerged pipe entry, (i.e. zero drop height), and sequentially increasing headspace ventilation rates. Stripping efficiencies, system mass transfer coefficients, and upper-bound ratios of air entrainment to liquid flowrate were determined for each experiment.

System mass transfer coefficients generally increased with increasing Henry's law coefficient, with some variation amongst the most volatile compounds, for the three experiments involving a 1.0 m drop height. No trends were observed for the partially and fully-submerged entry experiments. Mass transfer coefficients were greatest for the 1.0 m drop experiments, with a maximum value of 4.5 hr⁻¹ for 1,1,1-trichloroethane. Maximum system mass transfer coefficients for partially and fully-submerged entry experiments were 0.12/hr and 0.012/hr, respectively, each for trichloroethane.

Analyses were completed to assess the ratio of entrainment rate (Q_e) to influent water flowrate (Q) assuming all stripping was caused by entrained air and bubbles were completely saturated at the end of their entrainment time. Estimates of Q_e/Q ranged from a minimum of 0.0035 (for fully-submerged entry) to 1.4 (for 1.0 m drop height).

The following conclusions are made as a result of this study:

- Emissions of VOCs at sewer drop structures are significantly affected by the product of headspace ventilation rate and compound Henry's law coefficient.
- For compounds of low volatility and/or poor sewer ventilation conditions, an assumption of infinite ventilation can lead to order-of-magnitude or more overestimates of VOC emissions.

- Emissions of VOCs from sewer drop structures can be significantly reduced by controlling headspace ventilation rates.
- Emissions of VOCs from drop structures are highly sensitive to drop height, and can be reduced by an order-of-magnitude or more if it is possible to operate a drop structure with submerged entry, as opposed to drop heights of 1 m or greater.
- Entrained air bubbles are likely to be an important mechanism for mass transfer at sewer drop structures, except under conditions of submerged pipe entry.
- For conditions similar to those tested in this study, gas-phase resistance to mass transfer is important for 1,2-dichlorobenzene and less volatile compounds.

The following recommendations are made as a result of this study:

- Drop height was observed to have a significant effect on VOC emissions from the pilot drop structure. It is recommended that two additional drop heights of 0.5 and 2.0 m be studied.
- Ventilation rate was observed to have a significant effect on VOC emissions from the pilot drop structure. Furthermore, many of the ventilation rates used in this study are believed to be conservative, i.e. greater than typically observed in industrial sewers. Thus, it is recommended that a series of gas tracer experiments be completed in industrial sewers to determine natural headspace ventilation rates. Since submerged entry systems appear to have low relative removal, even under high ventilation conditions, field testing of ventilation should be completed in operating systems characterized by significant drop heights.
- If the headspace ventilation rates determined from field studies are significantly lower than those used in this study, additional experiments should be completed at lower ventilation rates.
- Previous studies indicated that VOC emissions are sensitive to water flowrate, particularly when hydraulic residence time in a tailwater pool is significant (Corsi *et al.*, 1993). Thus, it is recommended that additional pilot experiments be completed with lower and higher water flowrates than those used in this study.
- Pilot experiments indicated that gas-phase resistance to mass transfer can be significant for some compounds under specific drop structure operating conditions. It is recommended that future experiments be completed to determine system mass transfer coefficients for oxygen, which can then be used for estimating ratios of gas to liquid-phase mass transfer coefficients and resistances to mass transfer for each volatile tracer.
- It is not currently possible to determine the relative importance of the various mechanisms associated with gas-liquid mass transfer at drop structures. Results

presented in this report suggest that entrainment of air in the tailwater below a drop may be a significant mechanism where appreciable drop heights are present. It is recommended that a small flux chamber be added to the pilot drop structure in order to estimate both the amount of air entrained in a tailwater pool and the degree of saturation of rising bubbles with respect to various volatile compounds.

Measurement of HAP Emissions From Process Drains:

Nine experiments were conducted to measure HAP emissions from a pilot scale structure simulating a sewer and process drain connection. The sewer consisted of a 50 foot length of 4 inch diameter steel pipe. The drain consisted of a 4 inch diameter hub drain connected to the sewer by either a straight four inch pipe or a pipe with a p-trap. Experiments were conducted with no process wastewater flow into the drain and flowrates of 10% and 33% of the sewer flowrate. Tap water dosed with four VOCs and methanol was used as both the process and sewer wastewater. The wastewater was continuously recycled during the experiments. A flux box was utilized to simulate a 7 km/h (4.2 MPH) wind blowing over the open drain.

Since wastewater was continually recycled throughout the experiments, the concentration of HAPs in the wastewater would decline if there were significant emissions (like a batch process). For each experiment, effective mass transfer coefficients (k_L) were calculated based on the observed decline in wastewater concentration. In addition, sampling of the flux box effluent air was used for direct measurement of the HAP emission rates. Effective mass transfer coefficients were also derived using the gas sampling results. Except for two experiments, there was good agreement between mass transfer coefficients measured using gas samples $k_L(G)$ and mass transfer coefficients calculated based on the decline in the wastewater concentration $k_L(L)$ during the experiment. For two experiments, in which the measured HAP emission rate was small (p-trap, no process water flow into drain), $k_L(L)$ values were significantly higher than $k_L(G)$ values. It is postulated that $k_L(G)$ better represented the actual mass transfer coefficient, when drain emission rates were small, because $k_L(L)$ was inflated by emissions from other sources (i.e. small leaks within the system).

The following conclusions are made as a result of this study:

- For the system studied, significant ventilation was observed within the sewer pipe when a straight pipe connection was used between the drain and the sewer. Airflow velocities greater than 1 m/s were observed in the sewer. The ventilation resulted from the combined effects of liquid drag and wind eduction.
- The p-trap provided an effective vapor seal, minimizing the air velocity within the sewer pipe to less than 0.2 m/s. The airflow likely resulted from swirling within the sewer headspace rather than a net movement of air.
- There was no significant decline in the wastewater concentration of methanol during any experiment, and methanol was not observed in any gas sample. Maximum mass

transfer coefficient values (less than 1 E-2 h^{-1}) were calculated based on the analytical method detection limit for methanol in air.

- For all four VOCs, mass transfer coefficients were consistently less than 1 E-2 h^{-1} for the experiments in which the p-trap was in place with no process wastewater flow into the drain. Thus, the installation of p-traps could significantly reduce HAP emissions from process drains under some operating conditions. However, mass transfer coefficients increased significantly with process wastewater flow into the drain. It is postulated that mass transfer was induced by air blowing across the falling liquid stream, above the drain mouth, and possibly by air swirling above the p-trap and splashing water. Mass transfer coefficients also increased with increasing compound volatility.
- With a straight pipe connection (no p-trap) and no process water flow into the drain, the mass transfer coefficients of the VOCs were consistently greater than 0.1 h^{-1} . It is postulated that emissions were induced by mass transfer between the water in the sewer and the overlying air drawn up the drain pipe. For the single experiment carried out, there was no observed effect of compound volatility on the mass transfer coefficients.
- Process water flowrate into the drain did not have a consistent effect on mass transfer coefficients when a straight drain pipe (no p-trap) was in place. However, mass transfer coefficients increased with increasing compound volatility. It is postulated that emissions were induced by three combined effects:
 - mass transfer between water in sewer and overlying air drawn up drain pipe
 - stripping caused by wind blowing across the falling liquid above the drain mouth
 - mass transfer between swirling air above p-trap and splashing water

The following recommendations are made as a result of this study:

- A statistical analysis of the data presented in this report is recommended. Confidence intervals for the mass transfer coefficients should be calculated. More experiments may be required to achieve more narrow confidence intervals.
- For experiments in which the HAP emission rates were small (p-trap, no process wastewater flow into drain), there was a discrepancy between mass transfer coefficients calculated based on the decline in wastewater concentration ($k_L(L)$) and those calculated using gas samples ($k_L(G)$). This discrepancy should be resolved. Efforts should be made to further reduce miscellaneous leaks and experiments repeated.
- The impact of the location of the drop pipe in the drain on mass transfer coefficients should be investigated. It was postulated that significant emissions resulted from air blowing across the falling liquid, above the drain mouth. The impact of lowering the drop pipe below the drain mouth should be experimentally determined.

- Pilot scale experiments should be conducted under the range of operating conditions likely to be experienced at full scale. These conditions include:
 - sewer pipe length and diameter
 - drain pipe length and diameter
 - length of pipe between drain and p-trap
 - wastewater level in sewer pipe
 - process wastewater and sewer wastewater temperature
 - wind velocities
- Emission data should be collected from full scale operating drains. Flux boxes can be constructed around the drain for the collection of gas samples. The data collected can be compared to pilot scale data and also used for the calibration of mechanistic models.
- A mechanistic model for predicting HAP emissions from process drains should be developed. If complete mechanistic modelling is not possible, semi-empirical models should be derived using the data obtained from the experiments recommended above.

TABLE OF CONTENTS

VOLUME I

I.1 INTRODUCTION	I.1
I.2 MATHEMATICAL MODELS	I.3
I.2.1 LUMPED MECHANISM MODEL	I.3
I.2.2 ENTRAINMENT DOMINATED MODEL	I.4
I.3 METHODOLOGY	I.7
I.3.1 EXPERIMENTAL SYSTEM	I.7
I.3.2 SAMPLE ANALYSIS	I.10
I.3.3 EXPERIMENTAL PROCEDURE	I.11
I.3.4 EXPERIMENTAL PLAN	I.12
I.4 RESULTS AND DISCUSSION	I.14
I.4.1 DEGREE OF MASS CLOSURE	I.14
I.4.2 STRIPPING EFFICIENCY	I.15
I.4.3 SYSTEM MASS TRANSFER COEFFICIENTS	I.17
I.4.4 EFFECTS OF HEADSPACE VENTILATION	I.17
I.4.5 EFFECTS OF DROP HEIGHT	I.20
I.4.6 AIR ENTRAINMENT AS A MASS TRANSFER MECHANISM	I.20
I.5 SUMMARY AND CONCLUSIONS	I.22
I.6 RECOMMENDATIONS	I.23

VOLUME II

II.1 INTRODUCTION	II-1
II.1.1 PROCESS VARIABLES	II-2
II.2 MATERIALS AND METHODS	II-3
II.2.1.1 APPARATUS	II-3
II.2.1.2 SAMPLING AND ANALYTICAL METHODS	II-8
II.2.1.3 DOSING PROCEDURE	II-8
II.3 EXPERIMENTAL PLAN	II-9
II.4 RESULTS AND DISCUSSION	II-11
II.4.1 VENTILATION RATE	II-11
II.4.2 ANALYTICAL QUALITY ASSURANCE	II-13
II.4.3 EMISSION RATES	II-16

TABLE OF CONTENTS (Continued)

II.4.3.1 FORCED VENTILATION EXPERIMENTS	II-16
II.4.3.2 FREE VENTILATION EXPERIMENTS: P-trap Connection	II-19
II.4.3.3 FREE VENTILATION EXPERIMENTS: Straight Pipe Connection	II-31
II.4.4 COMPARISON OF EMISSION RATES	II-38
II.5 MASS TRANSFER RATE SUMMARY	II-40
II.6 SUMMARY AND CONCLUSIONS	II-47
II.7 RECOMMENDATIONS	II-49

APPENDICES

REFERENCES

Appendix I-A Drop Structure Experimental Data

APPENDIX II-A Analytical Methods

LIST OF FIGURES

VOLUME I

Figure I.1: Pilot Plant Schematic	I.8
Figure I.2: Physical Characteristics of Pilot Drop Chamber	I.9
Figure I.3: Stripping Efficiency Versus Headspace Ventilation	I.19

VOLUME II

Figure II.2.1: Schematic of Apparatus	II-5
Figure II.2.2: Schematic of Sewer Outlet	II-6
Figure II.2.3: Schematic of Drain Connection	II-7
Figure II.4.1: Experiment 3 - Plot of $\ln C_L$ vs Time	II-23
Figure II.4.2: Experiment 4 - Plot of $\ln C_L$ vs Time	II-24
Figure II.4.3: Experiment 5 - Plot of $\ln C_L$ vs Time	II-25
Figure II.4.4: Experiment 6 - Plot of $\ln C_L$ vs Time	II-26
Figure II.4.5: Experiment 7 - Plot of $\ln C_L$ vs Time	II-33
Figure II.4.6: Experiment 8 - Plot of $\ln C_L$ vs Time	II-34
Figure II.4.7: Experiment 9 - Plot of $\ln C_L$ vs Time	II-35
Figure II.5.1: Impact of Experimental Conditions On Mass Transfer Coefficients	II-44
Figure II.5.2: Impact of Particular Compound On Mass Transfer Coefficients	II-45

LIST OF TABLES

VOLUME I

Table I.1: Experimental Operating Conditions	I-13
Table I.2: Summary of Experimental Results	I-16

VOLUME II

Table II.2.1: Summary of Analytical Methods	II-8
Table II.3.1: Experimental Operating Conditions	II-10
Table II.4.1: Induced Air Velocity During Free Ventilation Experiments	II-12
Table II.4.2: Blank Gas Sample Analysis Results	II-13
Table II.4.3: Comparison of Duplicate Wastewater Samples	II-14
Table II.4.4: Comparison of Duplicate Off-gas Samples	II-15
Table II.4.5: Raw Data Summary - Experiment 1	II-17
Table II.4.6: Raw Data Summary - Experiment 2	II-17
Table II.4.7: Emission Rate Summary Forced Ventilation Experiments	II-18
Table II.4.8: Raw Data Summary - Experiment 3	II-20
Table II.4.9: Raw Data Summary - Experiment 4	II-20
Table II.4.10: Raw Data Summary - Experiment 5	II-21
Table II.4.11: Raw Data Summary - Experiment 6	II-21
Table II.4.11: Emission Rate Summary - Free Ventilation With P-Trap Drain Connection	II-29
Table II.4.12: Raw Data Summary - Experiment 7	II-31
Table II.4.13: Raw Data Summary - Experiment 8	II-31
Table II.4.14: Raw Data Summary - Experiment 9	II-32
Table II.4.15: Emission Rate Summary - Free Ventilation With Straight Pipe Drain Connection	II-37
Table II.4.16: Range and Median Emission Summary Calculated from Gas Measurements	II-39
Table II.5.1: Summary of Mass Transfer Rates ($k_L(G)$)	II-43

INTRODUCTION

The emission of hazardous air pollutants (HAPs) from industrial wastewater collection and treatment systems is becoming an increasing concern to regulatory authorities. There has been significant work to quantify emission rates from wastewater treatment systems, but relatively few studies on emissions from collection systems. In particular, there has been little investigation of fugitive emissions from collection system components. Two collection system components that are potential emissions sources are drop structures and process drain connections.

In September 1992, Enviromega, in cooperation with the Wastewater Technology Centre and the University of Guelph School of Engineering, commenced an experimental investigation of fugitive hazardous air pollutant (HAP) emissions from drop structures and process drains. Pilot scale structures were constructed to simulate full scale operating conditions. Tap water, dosed with representative HAPs, was used as wastewater. Both wastewater and off-gas samples were analyzed for the dosed HAPs, allowing for a direct measurement of emission rates. The emission rates measured during these studies are site specific and should be applied with prudence, especially given the potential complexity of individual collection systems. Simple emission factors should not be derived. Mass transfer coefficients measured during these studies can be used to calibrate models for predicting HAP emissions from wastewater collection systems.

Volume I of this report presents results from the investigation of HAP emissions from sewer drop structures. Volume II presents results from the investigation of HAP emissions from process drains.

VOLUME I

MEASUREMENT OF HAP EMISSIONS FROM SEWER DROP STRUCTURES

1.1 INTRODUCTION

Gas-liquid mass transfer of volatile organic compounds (VOCs) and semi-VOCs can be classified as occurring at two general locations in wastewater collection systems: 1) along relatively-uniform flowing sewer reaches, e.g. interceptor channels, and 2) at points of rapid dissipation of potential energy, e.g. drop manholes or free-fall drops into pump station wet wells (Corsi and Whitmore, 1992; Whitmore, *et al.*, 1992; Corsi *et al.*, 1992b). In either case, the rate of gas-liquid mass transfer between wastewater and a sewer atmosphere can be represented mathematically as:

$$R_v = -K_L \left(C - \frac{C_g}{H_c} \right) A \quad (1)$$

where:

- R_v = mass transfer rate across wastewater-air interface (mg/hr)
- K_L = overall mass transfer coefficient (m/hr)
- C = concentration of contaminant in the liquid phase (mg/m³)
- C_g = concentration of contaminant in the gas phase (mg/m³)
- H_c = compound-specific Henry's law coefficient ([mg/m³]_{gas}/[mg/m³]_{liq})
- A = area of wastewater-air interface (m²).

According to two-film theory, the inverse of the overall mass transfer coefficient can be written in terms of liquid- and gas-phase mass transfer resistances such that:

$$\frac{1}{K_L} = \frac{1}{k_l} + \frac{1}{k_g H_c} \quad (2)$$

where:

- k_l = liquid-phase mass transfer coefficient (m/hr)
- k_g = gas-phase mass transfer coefficient (m/hr).

Several mechanisms can contribute to gas-liquid mass transfer at sewer drop structures. Mass transfer can occur at:

- a. the free-falling wastewater surface
- b. splashing and airborne droplets generated at the tailwater surface
- c. agitated tailwater surface
- d. air bubbles entrained in the tailwater.

However, experimental separation of these mechanisms is complex, and methods to predict the contribution of each mechanism have not been reported. For these reasons, existing models of mass transfer at drop structures are highly empirical (Apted and Novak, 1973; Avery and Novak, 1978; Nakasone, 1986; Pincince, 1991), and general extrapolation of these models is characterized by a high degree of uncertainty.

1.2 MATHEMATICAL MODELS

1.2.1 LUMPED MECHANISM MODEL

A lumped mechanism model (LMM) for mass transfer at drop structures is based upon application of Equation 1, with an assumption that overall mass transfer can be "lumped" into a single "system" mass transfer coefficient K_L . This is analogous to applications for surface aerators, in which mass transfer caused by entrained air, airborne droplets and surface agitation are effectively accounted for using a single mass transfer coefficient. Interfacial area (A) is generally not known for such systems, except for quiescent surfaces and no entrained air. Thus, $K_L a$ values are obtained by dividing the product $K_L A$ by reactor volume V ($a = A/V$) and solving for $K_L a$ directly using data from batch reactor experiments. Therefore, $K_L a$ (oxygen) and $K_L a$ (VOC) values for drop structures are system-specific and highly dependant on both system geometry and localized non-uniformities in interfacial contact area.

If it is assumed that mass transfer to/from a falling wastewater is negligible compared to stripping caused by entrained air and splashing in a tailwater, C in Equation 1 can be replaced by the downstream concentration C_2 . Simultaneous solutions of steady-state mass balances on the gas and liquid phases of an enclosed drop structure, assuming a completely mixed tail water and headspace, lead to (Corsi *et al.*, 1993):

$$FractionStripped = 1 - \frac{C_2}{C_1} = \frac{1}{(1 + K_L a \theta_H f)} \quad (3)$$

- C_1 = contaminant concentration in wastewater at the top of a drop (mg/m^3)
- C_2 = contaminant concentration in tailwater at the bottom of a drop (mg/m^3)
- a = specific area = A/V ($1/\text{m}$)
- θ_H = hydraulic residence time (HRT) in the tailwater = V/Q (hr)
- K_L = overall system mass transfer coefficient (m/hr).

The parameter f is a factor that accounts for finite ventilation of the drop structure headspace and is equal to:

$$f = \left\{ 1 - \frac{1}{\frac{Q_g H_c}{V K_L a} + 1} \right\} \quad (4)$$

where:

- V = headspace volume (m^3)
- Q_g = headspace ventilation rate (m^3/hr)

Equation 4 indicates that an infinite ventilation condition can be approached, or reasonably assumed, if the product of $Q_g H_c$ is large, or $V K_L a$ is small.

The value of $\{1 - C_2/C_1\}$ is a measure of the amount of contaminant lost from wastewater by stripping at a drop structure, and can be estimated if liquid flowrate, tailwater volume, headspace ventilation rate, Henry's law coefficient, and $K_L a$ are known or reasonably estimated. For most applications, an accurate value for $K_L a$ is the limiting factor to applying Equation 4.

Steady-state mass balances on the gas and liquid phases of an enclosed drop structure can be used to estimate $K_L a$ based on field or pilot experiments. (Corsi *et al.*, 1993). Resulting equations based on liquid phase (Equation 5) and gas phase (Equation 6) mass balances are:

$$K_L a = \frac{C_1 - C_2}{\theta_H \left\{ C_2 - \frac{C_g}{H_c} \right\}} \quad (5)$$

$$K_L a = \frac{Q_g C_g}{\left\{ C_2 - \frac{C_g}{H_c} \right\} V} \quad (6)$$

Field measurements or the use of controlled tracer injections allow knowledge of C_1 , C_2 , and C_g . Values of V and Q_g can be measured or controlled, and H_c can be estimated from the literature if wastewater temperature is known (Ashworth *et al.*, 1988). Thus, application of Equations 5 or 6 allows estimates of system-specific mass transfer coefficients.

1.2.2 ENTRAINMENT DOMINATED MODEL

Entrainment dominated models (EDM) are based on the assumption that mass transfer at drop structures is due entirely to air bubbles entrained in tailwater. Corsi *et al.* (1993) derived the following equation for stripping efficiency at an enclosed drop structure during steady-state conditions:

$$\text{FractionStripped} = 1 - \frac{C_2}{C_1} = 1 - \frac{1}{\left\{ 1 + \frac{Q_e \gamma H_c}{Q} \left[1 - \frac{1}{1 + \frac{Q_g}{Q_e \gamma}} \right] \right\}} \quad (7)$$

where:

Q_e = rate of air entrainment into tailwater (m^3/hr)
 γ = degree of saturation of air bubbles exiting a tailwater surface (-).

All other variables are as described previously. Here, γ can take on values ranging from 0 to 1.

Equation 7 indicates the significance of entrained air bubbles in tailwater, liquid flowrate into a drop structure, and headspace ventilation rate. The denominator includes the ratio Q_e/Q . As this ratio becomes very large, i.e. large surface area associated with significant air entrainment and/or long HRT in tailwater, contaminant stripping from the drop system can be very high. The bracketed term within the denominator accounts for finite ventilation conditions, and entrainment of partially-saturated bubbles into a tailwater. If Q_e is held constant, the bracketed term approaches unity (infinite ventilation) as Q_g increases. Otherwise, the term is less than unity leading to smaller values of C_2/C_1 . This reflects a retardation of mass transfer, and subsequent reduction in emissions, caused by gaseous accumulation in the drop structure headspace.

Steady-state mass balances on the gas and liquid phases of an enclosed drop structure can be used to solve for the rate of air entrainment, assuming that it is the dominant removal mechanism (Corsi *et al.*, 1993). Resulting equations for the liquid (Equation 8) and gas (Equation 9) phases are:

$$Q_e = \frac{Q(C_1 - C_2)}{\gamma(C_2 H_c - C_g)} \quad (8)$$

$$Q_e = \frac{Q_g C_g}{\gamma(C_2 H_c - C_g)} \quad (9)$$

The major limitation to using Equations 8 and 9 to estimate Q_e is a lack of published information or methodology for estimating the degree of saturation term γ . It is conceivable that this value could be close to unity for contaminants with very low values of H_c , since only a small mass is then required in a rising bubble before it reaches saturation. Roberts *et al.* (1984) provided a mathematical expression to estimate the

degree of saturation of rising air bubbles in a conventional diffused bubble aeration system, given some simplifying assumptions, e.g. constant bubble diameter. However, the associated boundary conditions and simplifying assumptions may not be valid for air entrainment in a drop structure tailwater.

I.3 METHODOLOGY

In total, eight experiments were completed in a pilot drop structure to determine stripping efficiencies, lumped system mass transfer coefficients ($K_L a$) and air entrainment rates (Q_e) for five volatile organic compounds and methanol. The experimental system and methodologies are described below.

I.3.1 EXPERIMENTAL SYSTEM

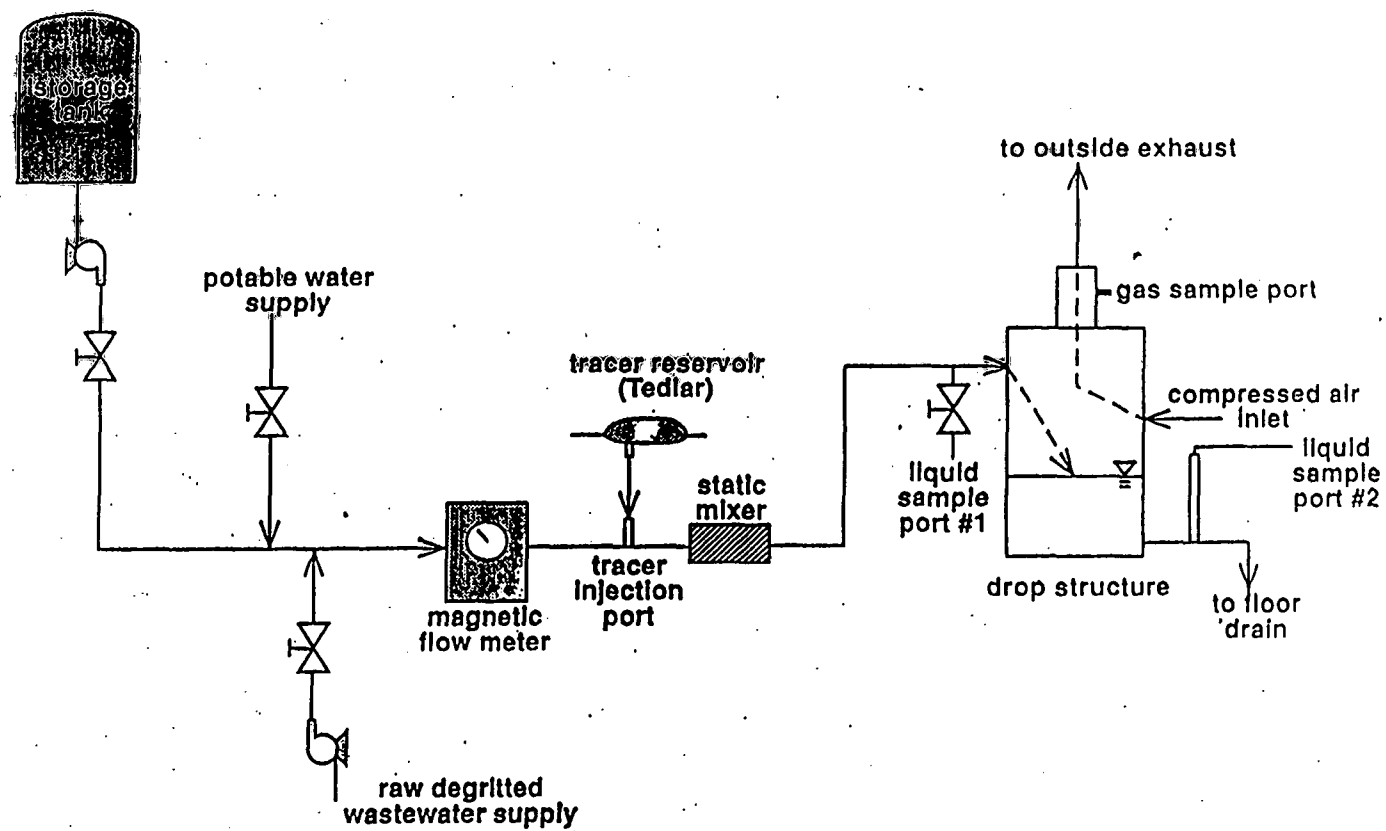
A pilot-scale drop structure was constructed at the Wastewater Technology Centre (WTC) in Burlington, Ontario. An illustration of the entire experimental system is provided in Figure I.1. The system consisted of five major components: water supply system, HAP injection system, enclosed drop chamber, headspace ventilation system, and sample collection system. Each of these components is described below.

For this study, a 68 m³ (18,000 US gallon) storage tank was filled with heated tap water, and recirculated by pumping during storage to maintain an elevated temperature. During experiments, water was pumped from the storage tank with the flowrate monitored and controlled by a magnetic flowmeter and pneumatic controller, respectively.

Five volatile compounds were used as representative HAPs during each experiment. These included 1,2-dichlorobenzene (DCB), toluene (TOL), trichloroethene (TCE), 1,1,1-trichloroethane (TCA) and tetrachloroethene (PERC). Methanol (METH) was also used as a less-volatile tracer in all but the last two experiments. Prior to and during each experiment, all tracer compounds were stored in a 25 L collapsible Tedlar^R reservoir which allowed the maintenance of a zero headspace. Representative HAPs were pumped from the bag using a peristaltic pump and 6 mm i.d. Teflon transport tubing. During experiments, the representative HAP solution was injected immediately upstream of a static mixer through a 6 mm i.d. stainless-steel tube extending into the pressurized water supply. Following the static mixer, the water/tracer solution was pumped to a 3 m long enclosed gravity-flow entrance pipe (PVC) connected to the drop chamber.

A schematic of the pilot drop chamber is provided in Figure I.2. The chamber consisted of a cylindrical, fibreglass tank with a height of 3.0 m and an internal diameter of 1.5 m. Water flowed into the chamber, over a drop, and accumulated in the base (tailwater) of the chamber before exiting to a floor drain. Tailwater depth was controlled through vertical adjustments of a flexible hose attached to the effluent pipe. Three flanges of 15 cm i.d. were staggered around the perimeter of the chamber at heights of 1.2 m, 1.8 m, and 2.5 m, measured as the distance from an entry pipe invert to the chamber floor. An influent water pipe could be connected to any of these entrances to maintain a constant drop height. The other entries were sealed when not in use.

Figure I.1: Pilot Plant Schematic



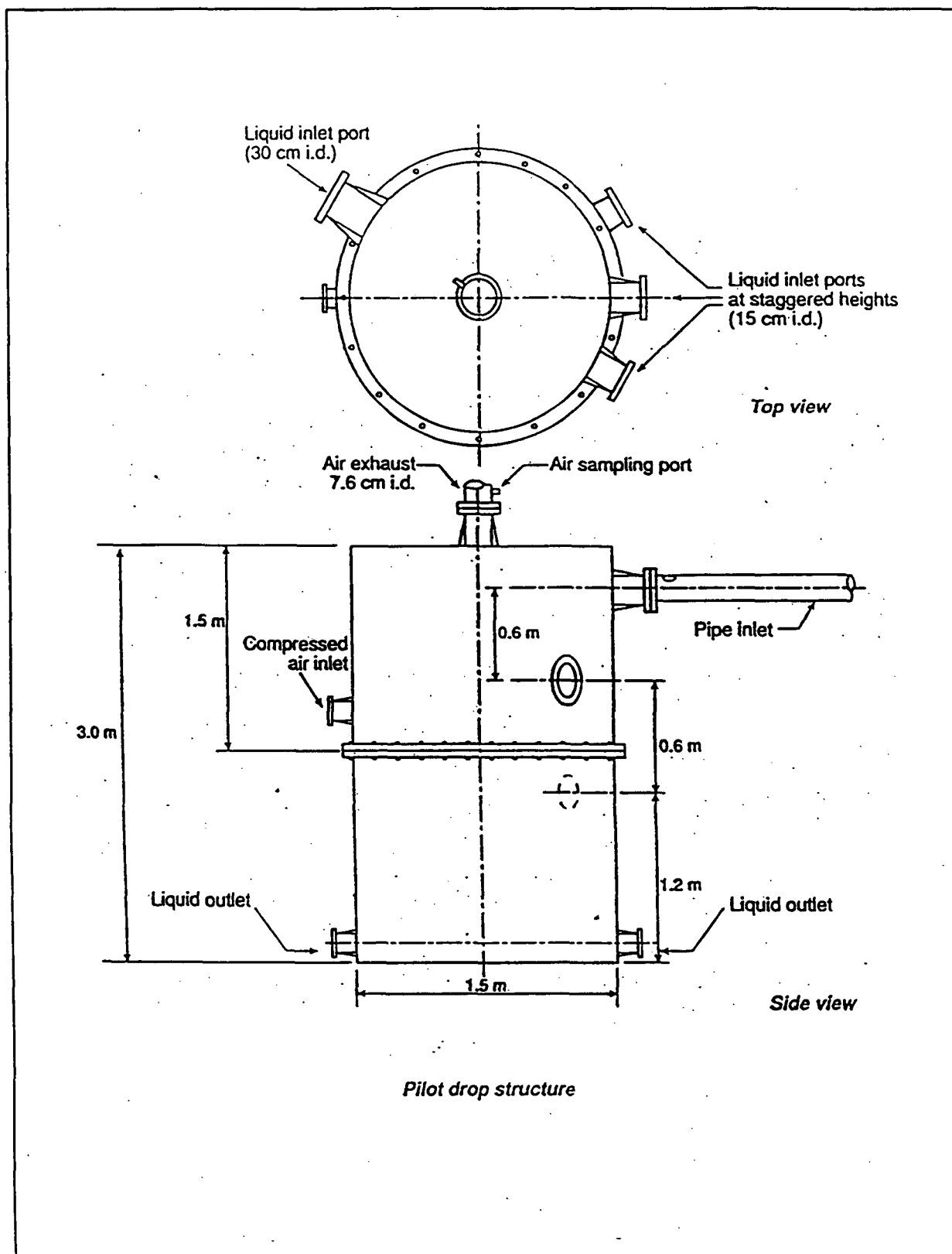


Figure I.2: Physical Characteristics of Pilot Drop Chamber

Compressed air was supplied to the drop chamber headspace to simulate the natural ventilation which can occur in wastewater collection systems and related hydraulic structures. The air flowrate was regulated using a rotameter upstream of its entry into the drop chamber headspace (at a height of 1.8 m above the chamber floor). Air flowrate was verified using a hot-wire anemometer (Airflow model TA2) which was inserted into the drop chamber exhaust vent. Velocity measurements were made at various points across the vent diameter to confirm a "flat" profile consistent with turbulent flow conditions.

The experimental system consisted of three sampling locations: 1) liquid sample valve immediately upstream of water entry into the drop chamber, 2) liquid sample riser pipe located immediately downstream of water discharge from the drop chamber, and 3) gas sample port on the exhaust vent. The latter was used for insertion of adsorbent tubes to collect headspace gas samples.

1.3.2 SAMPLE ANALYSIS

Both liquid and gaseous methanol samples were analyzed by the Wastewater Technology Centre laboratory using GC/FID. All other samples were analyzed in the Trace Contaminants Analysis Laboratory at the University of Guelph as described below.

Liquid samples were each injected into a 10 ml sparging vessel prior to concentration on to a Carbotrap 300 adsorbent tube connected to the only exhaust arm on the vessel. The sample was purged at 100 ml/min for 10 minutes using charcoal-polished ultra-high purity (UHP) nitrogen. Previous analyses indicated that a purge volume of one liter was sufficient to remove all volatile compounds from solution without causing breakthrough of the adsorbent tube.

A sixteen-tube Tekmar Aero autosampler was used for thermal desorption of all adsorbent tubes. The autosampler was plumbed to a Tekmar LSC 2000 purge and trap (PAT) system for internal concentration on a VOCARB 4000 focusing trap. The LSC 2000 was coupled to a Hewlett Packard 5890 series II gas chromatograph (GC) oven connected to a Hewlett Packard 5971 Mass Selective Detector (MS).

The autosampler method involved a 7.00 minute dry purge of each sample tube with charcoal polished UHP helium at a rate of 100 ml/min. This was followed by a 2.50 minute sample preheat to 200 °C and sample desorption for 3.25 minutes. The VOCARB focusing trap was then dry-purged at 100 ml/min for 2.50 minutes, preheated to 195 °C and desorbed for 2.50 minutes at 200 °C.

The GC was equipped with a DB-5 capillary column (30 m in length, 0.32 mm o.d., 1.0 mm film thickness). The GC was set to room temperature during desorption of the focusing trap. All lines and valve temperatures were maintained at 150 °C. The GC ramping method consisted of a constant temperature of 31 °C maintained for 2.50 minutes, ramp at 40 °C/min to 40 °C with a 1.0 minute hold, ramp at 9 °C/min to 120 °C, and ramp at 40 °C/min to 200 °C with a 2.00 minute hold.

The MS detector was optimally tuned for bromofluorobenzene. All samples were analyzed in selected ion monitoring (SIM) mode. Commercial standard mixtures (Supelco VOC mixes 7 and 8) were used to develop three- to five-point external calibration curves for each target analyte. Calibration curves were generally characterized by R^2 values between 0.95 and 0.999.

1.3.3 EXPERIMENTAL PROCEDURE

The cocktail of representative HAPs was prepared and stored in the Tedlar^R reservoir 24 hours in advance of each experiment. During preparation, the bag was first evacuated of all air prior to being filled with at least 20 L of tap water using a peristaltic pump and Teflon[®] transport tubing. During the filling procedure, precise quantities of each volatile tracer were injected using a gas-tight syringe punctured into the transport tubing immediately upstream of its connection with the Tedlar bag's entry valve. Following volatile tracer injection, five liters of reagent grade methanol were pumped directly into the Tedlar[®] reservoir.

Drop structure influent wastewater samples were taken downstream of the tracer injection location, following a static mixer. These values were used in the mass balance calculations. Thus, there was no reliance on a calculated influent HAP concentrations based on Tedlar bag content. However, our past experience has indicated that the concentration of volatile compounds (excluding ethylene dibromide which was not used in these experiments) contained in a Tedlar^R bag with a water/methanol mixture is stable over periods as long as twelve hours. The relatively low standard deviations of triplicate samples taken throughout the experiment (Appendix IA) confirm this observation.

During the start of each experiment, desired water flowrate, tailwater depth, and headspace ventilation rates were established and recorded. Following the collection of background samples (upstream liquid, downstream liquid, and chamber headspace), tracer injection was initiated at a pre-set injection rate (usually 40 ml/min), and initial injection time was recorded. Resulting upstream liquid concentrations generally ranged from 55 to 70 mg/L for methanol, and 30 to 100 mg/m³ for the other volatile compounds. The system was allowed to reach a steady-state condition during a time period corresponding to a minimum of 3.5 hydraulic/aerodynamic residence times of the tailwater pool and chamber headspace.

At steady-state, at least three sequential liquid samples were collected upstream and downstream of the drop chamber. All liquid samples were collected with zero headspace in thermally-conditioned 40 mL amber vials with Teflon-lined screw caps. To quantify gaseous concentrations of the five volatile compounds, at least two steady-state gas samples were also collected from the exhaust vent sample port during each experiment. Gas samples were collected using Carbotrap 300 multi-bed adsorbent tubes (6 mm o.d., stainless steel walls) and SKC model 224-PCXR7 programmable air sampling pumps. A bubble flowmeter was used downstream of the adsorbent tube to quantify air flowrates and associated sample volumes drawn through each adsorbent tube. In general, sample flowrates varied from 30 ml/min to 120 ml/min, with sample volumes

varying from 100 to 1000 mL depending on headspace ventilation and anticipated gaseous VOC concentrations. During each experiment, one breakthrough, one trip blank and one field blank were used with levels always below method detection limits (generally less than 10 ng of tracer mass). Following sample collection, adsorbent tubes were capped at each end using stainless-steel plugs. Each tube was then placed in a hermetically sealed glass container and stored in an ice chest for transport to the University of Guelph. Once at the lab, adsorbent tubes were refrigerated at 4 °C until analysis.

In addition to the liquid and gas samples collected to quantify volatile tracer concentrations, samples were also collected for subsequent methanol analyses. Two upstream and two downstream steady-state liquid samples were collected during each experiment. Again, liquid samples were collected in 40 mL amber glass vials with Teflon-lined screw caps and zero headspace. Gas samples were collected in 1/2 inch o.d. glass methanol traps packed with 35/50 mesh magnesium silica. Air samples were collected using an SKC model 224-PCXR7 programmable sampling pump. Sample flowrates varied from 100 to 500 mL/min, with total sample volumes ranging from 2 to 4 L. Following sample collection, each methanol trap was sealed in its own plastic bag and stored in a refrigerator at 4 °C until analysis.

1.3.4 EXPERIMENTAL PLAN

Volatile tracer experiments were completed using eight system operating conditions as listed in Table I.1. Over all the experiments, liquid flowrate was maintained at 6.8 m³/hr (30 US gallons per minute).

Experiments 1-3 were characterized by a drop height of 1.0 m, tailwater depth of 0.5 m, and water temperatures ranging from 24 to 28 °C. For this set of experiments, headspace ventilation rates were sequentially increased from 2.7 to 27 m³/hr.

Experiments 4-6 were characterized by a tailwater depth of 1.3 m, with complete submergence (3 cm above crown) of the inlet pipe. For this set of experiments, water temperature was 23 °C, and headspace ventilation rate was sequentially increased from 2.7 to 27 m³/hr.

Experiments 7 and 8 were characterized by a partially-submerged inlet pipe, with a tailwater depth of 1.1 m extending approximately 2 cm above the invert of the inlet pipe. For these two experiments, water temperature was 25 °C, and headspace ventilation rate was varied from 5.4 to 27 °C.

Liquid temperatures recorded during each experiment were used to estimate Henry's law coefficients (H_c) for each VOC based on Ashworth *et al.* (1988). A functional relationship between temperature and methanol could not be found in the literature. Therefore, H_c (methanol) was assumed to be 6×10^{-4} (mg/m³ - gas)/(mg/m³ - liquid) at each experimental temperature.

Table I.1. Experimental Operating Conditions

Experiment #	Flowrates (m ³ /hr)		Drop Height (m)	Tailwater Depth (m)	Temp. (°C)	
	Liquid	Gas			Liquid	Gas
1	6.8	2.7	1.0	0.5	24	20
2	6.8	4.0	1.0	0.5	28	23
3	6.8	27	1.0	0.5	24	21
4	6.8	2.7	0 ^a	1.3	23	21
5	6.8	14	0 ^a	1.3	23	21
6	6.8	27	0 ^a	1.3	23	21
7	6.8	5.4	0 ^b	1.1	25	22
8	6.8	27	0 ^b	1.1	25	22

Notes:

- a. Influent pipe completely submerged. Water surface approximately 3 cm above crown (top) of pipe.
- b. Influent pipe partially submerged. Water surface approximately 2 cm above invert (bottom) of pipe.

I.4 RESULTS AND DISCUSSION

For each experiment, degree of mass closure, stripping efficiency, system mass transfer coefficient, and the product of air entrainment rate and degree of entrained bubble saturation were calculated for each volatile tracer. Experimental results are tabulated in Appendix IA, and summarized below.

I.4.1 DEGREE OF MASS CLOSURE

Degree of mass closure (MC) was defined by the following equation:

$$MC = \left\{ \frac{Q_s C_s + QC_2}{QC_1} \right\} \cdot 100 \quad (10)$$

Values of MC are listed in Table I.2 for each compound and experimental condition. Mass closures were generally good, ranging from a low of 73% to a high of 120%. Of 43 total MC values, 31 were within 10% of perfect mass closure (100%). A total of 40 out of 43 were within 20% of perfect mass closure. Eleven values of MC were greater than 100%, and two were equal to 100%. Over half of the mass closures less than 100% were between 96 and 99%.

For mass closures of less than 100%, estimates of $K_L a$ were greater based on Equation 5 as opposed to Equation 6. Similarly, stripping efficiencies estimated from mass removal from liquid (differences in mass flows upstream and downstream of drop) were greater than those estimated from mass flow in the exhaust gas stream relative to upstream liquid mass flow. However, differences in upstream and downstream liquid concentrations were small, often within analytical errors expected during sample analysis. Thus, they would have been expected to lead to significant uncertainties if they were used to estimate either $K_L a$ or stripping efficiency. Furthermore, although all transfer lines were made of Teflon, downstream liquid samples were collected using a peristaltic pump with silicone tubing in the pump head. It is conceivable that some tracer adsorption occurred in the pump head, leading to slightly lower tracer concentrations in downstream samples. Thus, for all analyses, values of stripping efficiency and $K_L a$ were based on mass removal rates equal to mass flows in the exhaust gas stream. For completeness, values of stripping efficiency and $K_L a$ based on both mass flowrates in exhaust gas and differences in upstream and downstream mass flowrates are provided in Appendix IA.

1.4.2 STRIPPING EFFICIENCY

Stripping efficiency (SE) was defined as:

$$SE = \left\{ \frac{Q_s C_s}{Q C_1} \right\} \cdot 100\% \quad (11)$$

Values of SE and Henry's law coefficient (H_c) are listed in Table 1.2 for each compound/experiment combination.

For all experiments, SE values for the least volatile compound (methanol) were less than 1%. For experiments 1-3, SE generally increased with increasing H_c , with some variation amongst the most volatile compounds (TCE, TCA, and PERC). There was no apparent trend between SE and H_c for the fully-submerged (4-6) and partially-submerged (7-8) experimental conditions.

Table I.2: Summary of Experimental Results

Expt #	Compound	H_c	% Stripped	K_{La} (1/hr)	Q_g/Q	MC (%)
1	Methanol	0.0006	< 0.02	< 0.016	< 0.33	97
1	1,2-Dichlorobenzene	0.075	2.1	0.69	1.2	96
1	Toluene	0.26	2.5	0.26	0.13	97
1	Trichloroethene	0.41	10	4.3	1.4	94
1	1,1,1-Trichloroethane	0.69	8.2	1.3	0.24	89
1	Tetrachloroethene	0.71	9.6	1.7	0.32	85
2	Methanol	0.0006	< 0.02	< 0.0021	< 0.46	105
2	1,2-Dichlorobenzene	0.078	< 0.07	< 0.00072	< 0.015	73
2	Toluene	0.29	5.6	0.77	0.34	94
2	Trichloroethene	0.46	10	2.2	0.63	83
2	1,1,1-Trichloroethane	0.78	21	4.5	0.75	102
2	Tetrachloroethene	0.84	15	2.3	0.37	96
3	Methanol	0.0006	< 0.3	< 1.2	< 265	120
3	1,2-Dichlorobenzene	0.075	6.6	0.80	1.4	93
3	Toluene	0.26	9.9	0.95	0.47	99
3	Trichloroethene	0.41	21	2.7	0.87	91
3	1,1,1-Trichloroethane	0.69	15	1.9	0.35	83
3	Tetrachloroethene	0.71	23	3.3	0.60	84
4	Methanol	0.0006	< 0.005	< 0.00016	< 0.09	110
4	1,2-Dichlorobenzene	0.074	0.2	0.0054	0.025	106
4	Toluene	0.26	0.2	0.0073	0.010	98
4	Trichloroethene	0.39	0.3	0.0077	0.007	99
4	1,1,1-Trichloroethane	0.66	0.2	0.0068	0.0035	99
4	Tetrachloroethene	0.68	0.3	0.0086	0.0043	99
5	Methanol	0.0006	< 0.02	< 0.00088	< 0.5	100
5	1,2-Dichlorobenzene	0.074	< 0.1	< 0.0038	< 0.015	93
5	Toluene	0.26	0.2	0.0056	0.007	101
5	Trichloroethene	0.39	0.4	0.012	0.011	96
5	1,1,1-Trichloroethane	0.66	0.3	0.0080	0.004	99
5	Tetrachloroethene	0.68	< 0.2	< 0.0047	< 0.002	101
6	Methanol	0.0006	NA	NA	NA	NA
6	1,2-Dichlorobenzene	0.074	< 0.3	< 0.0084	< 0.038	102
6	Toluene	0.26	< 0.3	< 0.0094	< 0.012	97
6	Trichloroethene	0.39	< 0.4	< 0.012	< 0.010	100
6	1,1,1-Trichloroethane	0.66	< 0.4	< 0.011	< 0.0056	99
6	Tetrachloroethene	0.68	< 0.4	< 0.012	< 0.0062	99
7	1,2-Dichlorobenzene	0.076	1.4	0.075	0.28	92
7	Toluene	0.27	1.9	0.11	0.11	73
7	Trichloroethene	0.42	2.3	0.12	0.078	79
7	Tetrachloroethene	0.75	2.0	0.085	0.032	88
8	1,2-Dichlorobenzene	0.076	1.2	0.052	0.19	89
8	Toluene	0.27	2.6	0.10	0.11	96
8	Trichloroethene	0.42	2.0	0.080	0.054	88
8	Tetrachloroethene	0.75	2.1	0.071	0.028	107

a: Units of H_c are $[\text{mg}/\text{m}^3 \text{ in gas phase}] / [\text{mg}/\text{m}^3 \text{ in liquid phase}]$.

Values of SE were generally greatest for experiments 1-3 (1 m drop height) and lowest for experiments 4-6 (fully-submerged entry). For experiments 1-3, SE for individual compounds generally increased with increasing headspace ventilation rate. This trend was not observed for the submerged entry conditions (experiments 4-8). Over all experiments, the maximum SE was 23% (PERC, experiment 3).

1.4.3 SYSTEM MASS TRANSFER COEFFICIENTS

Overall system mass transfer coefficients ($K_L a$) were calculated based on Equation 6. A discussion of the selection of equation 6, rather than equation 5, for the calculation of mass transfer coefficients is presented in Section 1.4.3. Values of $K_L a$ are listed in Table 2 for each compound/experiment combination. As with SE, $K_L a$ for experiments 1-3 generally increased with increasing H_c with some variation amongst the three most volatile compounds. There was no apparent trend between $K_L a$ and H_c for experiments 4-8.

Values of $K_L a$ were generally greatest for experiments 1-3 and lowest for experiments 4-6. Maximum values of $K_L a$ did not coincide with maximum SE, and were observed for TCA during experiment 2 ($K_L a = 4.5/\text{hr}$) and experiment 3 ($K_L a = 4.3/\text{hr}$).

1.4.4 EFFECTS OF HEADSPACE VENTILATION

The product of headspace ventilation rate and Henry's law coefficient, hereafter referred to as the headspace ventilation factor (HVF) appears in Equation 4. It serves as a measure of how far an enclosed drop structure is from infinite ventilation (open) conditions for a specific contaminant. For large values of HVF, f in Equations 3 and 4 approaches unity. Thus, all other factors being equal, SE should approach a constant infinite ventilation value as HVF increases.

Stripping efficiency is plotted versus HVF in Figure 1.3. Three separate symbols are used for data corresponding to experiments 1-3, experiments 4-6 and experiments 7 and 8. All stripping efficiencies reported as $< X\%$ in Table 1.2 are plotted as 0% in Figure 3. Best fit lines are also plotted through each set of data.

For experiments 1-3 there was a clear trend of increasing SE with increasing HVF. The experimental data appear to level off at approximately 15-20% at large HVF. Values of SE for experiments 7-8 appeared to level off between 2% and 2.5% at HVF greater than 2. Values of SE for experiments 4-6 were less than 0.5% for all values of HVF.

At $27 \text{ m}^3/\text{hr}$ for experiments 3, 6, and 8, headspace turnover rates were 6.1/hr, 9.0/hr, and 8.0/hr, respectively. These high ventilation rates would likely not be observed in most on-site industrial sewers. Exceptions might include force-ventilated sewers, near open sewers, rapid pump and fill wet wells, or sewers with many drain openings that are exposed to high wind speeds. For sewers that do not fall into any of these categories, maximum stripping efficiencies may be significantly lower than those reported here.

The results presented in Figure 1.3 illustrate the importance of properly quantifying both

chemical volatility, as measured by H_v , and headspace ventilation rate for predicting VOC emissions at drop structures. For compounds of low volatility and or/ poor sewer ventilation conditions, an assumption of infinite ventilation may lead to order-of-magnitude overestimates of VOC emissions.

Clearly, one method of reducing VOC emissions from drop structures is to control ventilation rates within such systems.

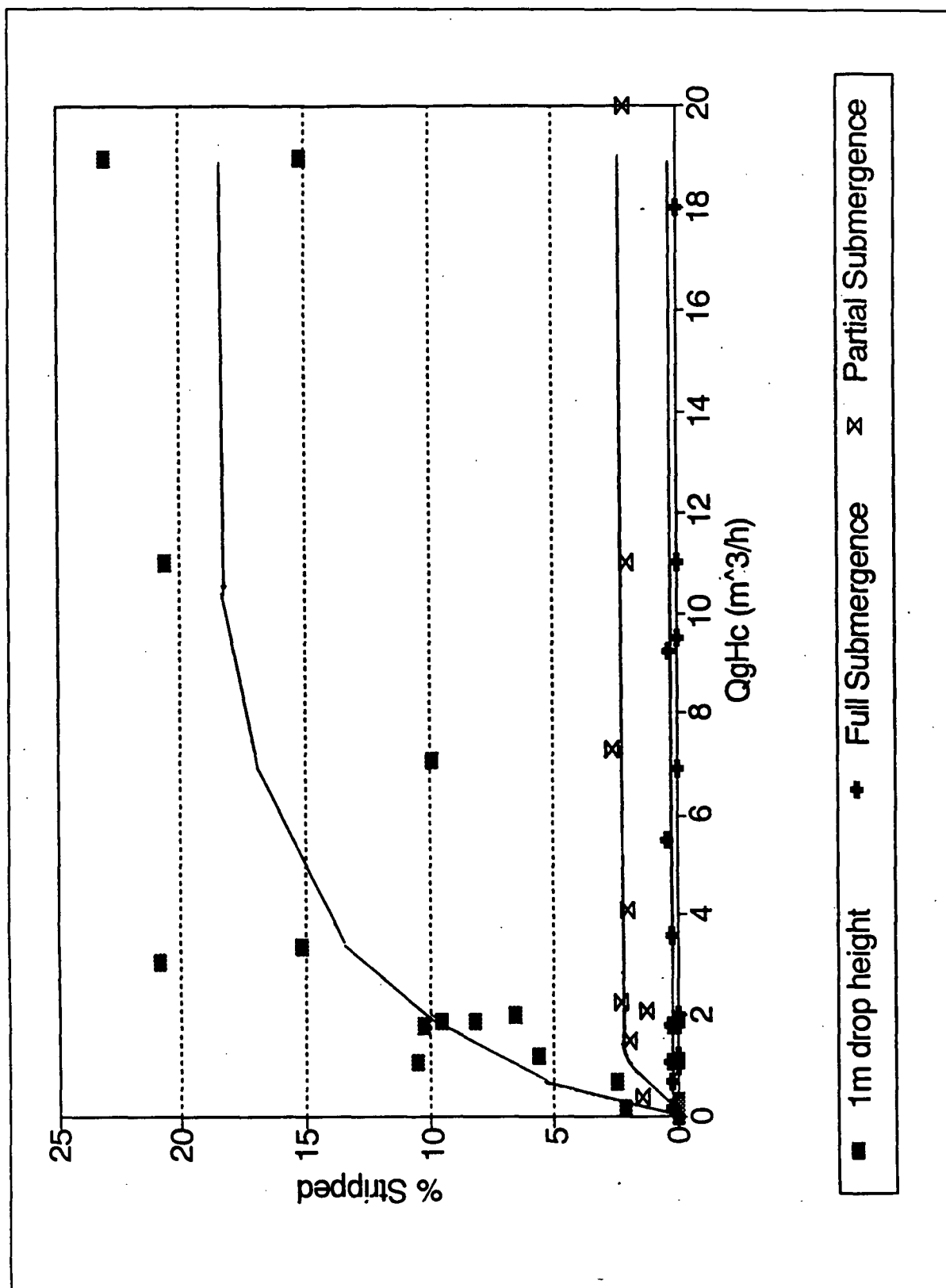


Figure I.3: Stripping Efficiency Versus Headspace Ventilation

I.4.5 EFFECTS OF DROP HEIGHT

Figure I.3 also illustrates the effect of drop height on VOC emissions at junction boxes and wet wells. For the experimental conditions tested in this study, VOC stripping efficiencies were generally reduced by a factor of 4 to 10 between the 1 m drop height and partially-submerged entry, and a factor of 10 to 20 between the 1 m drop height and fully-submerged entry.

Thus, another method for significantly reducing VOC emissions from junction boxes and wet wells is to operate with submerged, as opposed to free-fall, pipe entry into the system.

I.4.6 AIR ENTRAINMENT AS A MASS TRANSFER MECHANISM

Nakasone (1986) estimated that greater than 90% of oxygen transfer at a weir is due to air entrainment caused by falling water that impacts an underlying tailwater. Mclachlan *et al.* (1990) assumed that air entrainment at large waterfalls accounts for all emissions from such systems. Furthermore, they assumed that for all VOCs $\gamma = 1$ (bubbles fully saturated) and Q_a/Q varied from 5 to 30. These assumptions were used to estimate VOC emissions from Niagara Falls. Finally, Mihelcic *et al.* (1993) provided an example calculation of VOC emissions from a clarifier weir and assumed a Q_a/Q value of 0.03. No verification or argument to support this value was provided.

For the pilot experiments described in this report it was not possible to separate the values of Q_a and γ . However, conservative (upper-bound) estimates of Q_a/Q were determined using Equation 9, normalized by Q , and the following assumptions:

1. All emissions were caused by air entrainment.
2. Rising air bubbles were saturated ($\gamma = 1.0$) with respect to each tracer.

Because many values of C_g were less than detection limit for experiments 5 and 6, it was not possible to ascertain a trend between Q_a/Q and increasing H_c . This result was expected given that Q_a/Q should not be compound dependant, and γ should decrease with increasing H_c . For experiments 1-3, there was no apparent trend between Q_a/Q and H_c .

Omitting those values listed as "less than", Q_a/Q ranged over approximately two to three orders of magnitude for the eight pilot experiments. The highest values were 1.4 for TCE (experiment 1) and 1,2-DCB (experiment 3). The lowest observed value was 0.0035 (TCA, experiment 4). In general, the degree of air entrainment increased from fully-submerged to partially submerged and finally to a 1 m drop height. These results make intuitive sense, and also suggest a plausible explanation for SE dependency on H_c for the drop conditions (experiments 1-3), but not on experiments 4-8. Assuming that both gas-phase resistance to mass transfer and the amount of entrained air is small, SE should primarily be a function of compound diffusivities in the liquid phase. Thus, if such conditions were to exist, SE would be approximately the same for all compounds used in this study.

For the conditions in which air entrainment was expected to be small (experiments 4-8), values of SE were approximately equal, or at least not a strong function of H_c for all compounds other than the two least volatile compounds (methanol and 1,2-DCB). For methanol, SE was always less than all other compounds, indicating significant gas-phase resistance to mass transfer. This was also the case for 1,2-DCB for experiments 5, 7, and 8, indicating some gas-phase resistance to mass transfer even at very high ventilation rates. The apparent dependency of stripping efficiency on H_c for experiments 1-3 suggests that either gas-phase resistance to mass transfer and/or significant air entrainment must have occurred.

In summary, results indicate:

1. Gas-phase resistance to mass transfer is important for 1,2-DCB and less volatile compounds.
2. Air entrainment is not a significant emissions mechanism for submerged entry systems, but is likely to be an important emissions mechanism where substantial drops occur, e.g. the 1 m drop tested in this study.

1.5 SUMMARY AND CONCLUSIONS

Eight experiments were completed to study HAP emissions at sewer drop structures. Five VOCs and methanol were used as representative compounds. Water flowrate was held constant at $6.8 \text{ m}^3/\text{hr}$ for each experiment. Three experiments were completed with a drop height of 1.0 m, with sequentially increasing headspace ventilation rates. Five experiments were completed with either partially or fully-submerged pipe entry, (i.e. zero drop height), and sequentially increasing headspace ventilation rates. Stripping efficiencies, system mass transfer coefficients, and upper-bound ratios of air entrainment to liquid flowrate were determined for each experiment.

System mass transfer coefficients generally increased with increasing Henry's law coefficient, with some variation amongst the most volatile compounds, for the three experiments involving a 1.0 m drop height. No trends were observed for the partially and fully-submerged entry experiments. Mass transfer coefficients were greatest for the 1.0 m drop experiments, with a maximum value of 4.5 hr^{-1} for 1,1,1-trichloroethane. Maximum system mass transfer coefficients for partially and fully-submerged entry experiments were 0.12/hr and 0.012/hr, respectively, each for trichloroethene.

Analyses were completed to assess the ratio of entrainment rate (Q_e) to influent water flowrate (Q) assuming all stripping was caused by entrained air and bubbles were completely saturated at the end of their entrainment time. Estimates of Q_e/Q ranged from a minimum of 0.0035 (for fully-submerged entry) to 1.4 (for 1.0 m drop height).

The following conclusions are made as a result of this study:

- Emissions of VOCs at sewer drop structures are significantly affected by the product of headspace ventilation rate and compound Henry's law coefficient.
- For compounds of low volatility and/or poor sewer ventilation conditions, an assumption of infinite ventilation can lead to order-of-magnitude or more overestimates of VOC emissions.
- Emissions of VOCs from sewer drop structures can be significantly reduced by controlling headspace ventilation rates.
- Emissions of VOCs from drop structures are highly sensitive to drop height, and can be reduced by an order-of-magnitude or more if it is possible to operate a drop structure with submerged entry, as opposed to drop heights of 1 m or greater.
- Entrained air bubbles are likely to be an important mechanism for mass transfer at sewer drop structures, except under conditions of submerged pipe entry.
- For conditions similar to those tested in this study, gas-phase resistance to mass transfer is important for 1,2-dichlorobenzene and less volatile compounds.

1.6 RECOMMENDATIONS

The drop experiments presented in this report have provided valuable insight to the relative magnitudes of HAP emissions under various system operating conditions. Nevertheless, several additional experiments could be used to assess the relative importance of gas-liquid mass transfer mechanisms, and to establish emissions under a wider range of operating conditions. Recommendations for future research are presented below:

- Drop height was observed to have a significant effect on VOC emissions from the pilot drop structure. It is recommended that two additional drop heights of 0.5 and 2.0 m be studied.
- Ventilation rate was observed to have a significant effect on VOC emissions from the pilot drop structure. Furthermore, many of the ventilation rates used in this study are believed to be conservative, i.e. greater than typically observed in industrial sewers. Thus, it is recommended that a series of gas tracer experiments be completed in industrial sewers to determine natural headspace ventilation rates. Since submerged entry systems appear to have low relative removal, even under high ventilation conditions, field testing of ventilation should be completed in operating systems characterized by significant drop heights.
- If the headspace ventilation rates determined from field studies are significantly lower than those used in this study, additional experiments should be completed at lower ventilation rates.
- Previous studies indicated that VOC emissions are sensitive to water flowrate, particularly when hydraulic residence time in a tailwater pool is significant (Corsi *et al.*, 1993). Thus, it is recommended that additional pilot experiments be completed with lower and higher water flowrates than those used in this study.
- Pilot experiments indicated that gas-phase resistance to mass transfer can be significant for some compounds under specific drop structure operating conditions. It is recommended that future experiments be completed to determine system mass transfer coefficients for oxygen, which can then be used for estimating ratios of gas to liquid-phase mass transfer coefficients and resistances to mass transfer for each volatile tracer.
- It is not currently possible to determine the relative importance of the various mechanisms associated with gas-liquid mass transfer at drop structures. Results presented in this report suggest that entrainment of air in the tailwater below a drop may be a significant mechanism where appreciable drop heights are present. It is recommended that a small flux chamber be added to the pilot drop structure in order to estimate both the amount of air entrained in a tailwater pool and the degree of saturation of rising bubbles with respect to various volatile compounds.

VOLUME II**MEASUREMENT OF HAP EMISSIONS FROM PROCESS DRAINS**

II.1 INTRODUCTION

Wastewater generated during the manufacture of organic chemicals generally enters the collection and treatment system through a number of individual drains distributed throughout each unit process. Some drains may be dedicated to a single piece of equipment (e.g. a single pump), while others may serve several sources. These drains are connected to sewer lines. Drain lines or piping from the various sources generally terminate just within, or slightly above the mouth of the process drain. The connection between the drain and the sewer line frequently consists of a straight pipe, commonly 4-6 inches in diameter, that extends to a height 4-6 inches above grade. Alternatively, the connections consist of a pipe with a p-bend to provide a liquid seal between the sewer and the atmosphere.

There is the potential for hazardous air pollutant (HAP) emissions whenever there is an interface between a stream containing HAPs and the atmosphere. The individual drains within a wastewater collection system provide such an interface. Emissions can occur from the wastewater flowing through the sewers or as the wastewater is directed into the sewers. Factors affecting emission rate include the following:

- ventilation rate
- sewer mass transfer characteristics (length)
- process wastewater flow characteristics
- volatility of individual HAPs

The HAP emission rate will depend on the ventilation rate, or the rate of exchange between the contaminated air and the atmosphere, with emissions increasing as ventilation increases. HAP emission will also depend on the gas-liquid mass transfer characteristics of the sewer. These in turn will depend on the turbulence within the sewer. As the turbulence increases, the mass transfer rate and emission rate will also increase. The HAP emission rate will also depend on the characteristics of the flow through the drain into the sewer. Process wastewater flow into the drain may induce significant emissions by causing splashing within the sewer or emissions may be induced by wind blowing across the falling liquid between the end of the drain pipe and the mouth of the drain. Finally, the volatility of individual HAPs will also influence the magnitude of emissions.

The HAP emission rate from process drains is not well known. It is thought that P-trap connections reduce HAP emissions from the sewer line to a small percentage of the liquid mass HAP flowrate, although this has not been demonstrated. To this end, a pilot scale sewer and process drain were constructed to facilitate the measurement of emission rates. The system was designed to simulate potential full scale operating conditions to allow for a comparison of emission rates from drains connected with a straight pipe and a p-trap connection. A flux box was utilized to simulate a wind blowing over the open drain.

The emission rates measured from the pilot structure are site specific and should be applied with prudence, especially given the potential complexity of individual collection systems. Simple emission factors should not be derived. The measured mass transfer coefficients can be used for the calibration of predictive models of emissions from collection

systems presently being developed.

II.1.1 PROCESS VARIABLES

The impact of the following variables on HAP emissions from process drain connections was investigated:

- compound volatility
- drain connection (p-trap or straight pipe)
- process water flowrate into drain

The impact of compound volatility on emission rate was investigated by utilizing a mixture of compounds with varying Henry's Law coefficients. The impact of the type of drain connection was investigated by repeating experiments with interchangeable p-trap and straight pipe connections. Finally, experiments were conducted with no process wastewater flow into the drain and flowrates of 10% and 33% of the sewer flowrate.

II.2.1 MATERIALS AND METHODS

II.2.1.1 APPARATUS

The apparatus consisted of a sewer line, a process drain connection and a wastewater storage tank. A schematic is presented in Figure II.2.1. The wastewater was dosed with the HAPs before each experiment and recycled during the experiment. The same wastewater was used as both the sewer influent and as the discharge, through the process drain, into the sewer. The drain could be connected to the sewer by either a straight length of pipe or a pipe with a P-trap.

The sewer consisted of a 4 inch diameter carbon steel pipe with a slope of 1.8%. The sewer consisted of 40 feet of pipe upstream of the drain and 10 feet of pipe downstream of the drain. A 1 inch diameter sample port was drilled in the top of the sewer line for insertion of an anemometer for measuring airflow rate within the sewer. The sample port was plugged when not in use. The outlet of the sewer discharged into an 18 inch diameter overflow vessel. The top of the overflow vessel was sealed using a rubber gasket and steel cover. A two inch steel line discharged from the bottom of the overflow vessel into a 1.25 m³ fiberglass storage tank filled with wastewater. A detailed schematic of the sewer outlet is presented in Figure II.2.2. The wastewater storage tank was sealed using a rubber gasket and steel cover. A valve on the discharge line from the overflow tank to the storage tank controlled the liquid level in the main sewer at 2 inches.

Wastewater was pumped from the storage tank using a centrifugal pump. The pump discharge proceeded through a T-fitting. From the T, one of lines proceeded to the inlet of the sewer (sewer inlet line) and one line proceeded overhead to the drain connection (process water line). Both lines had rotameters for flow measurement and control valves. The sewer inlet line proceeded upwards into a T-connection. One end of the T was connected to the sewer using a flange and rubber gasket. The top end of the T was open to the atmosphere. This opening, at the inlet of the sewer, allowed air to enter the sewer.

The process water line rose vertically from the storage tank to ensure that it was full of water to provide a vapor seal. Once above the drain, it discharged vertically into the drain. The process line discharge was 1.5 " above the mouth of the drain (Figure II.2.3). The drain consisted of a 4 inch diameter hub train. The drain was connected to the sewer through either a straight 4 inch diameter pipe or a 4 inch diameter pipe with a P-trap. The height of the drain above the sewer was 6 feet.

Both the drain and process line discharge were surrounded by a 16 inch square galvanized steel flux box (Figure II.2.3). The entire length of the flux box was 6 feet. The front of the flux box was located 1.5 feet ahead of the drain. The flux box inlet could either be sealed or left open to the atmosphere. The outlet of the flux box was reduced gradually to four inches diameter. A gas sample port was located at the outlet end of the flux box. Air turbulence, caused by the reduction in size from 16 inch diameter to 6 inch diameter, was used to mix the off-gas sample. For experiments in which the sewer was force ventilated, the inlet to the flux box was sealed and a vacuum pump connected to the outlet of the flux

box to pull air from the sewer inlet, along the length of the sewer, up the straight pipe connection and out the discharge end of the flux box. The ventilation rate was measured with a rotameter at the outlet of the flux box. For experiments in which wind over the drain was simulated, the inlet to the flux box was left open and the outlet of the flux box connected to the inlet of a fan. The fan discharge was ventilated outside of the building. The wind flowrate was measured using an anemometer at various locations at the flux box inlet.

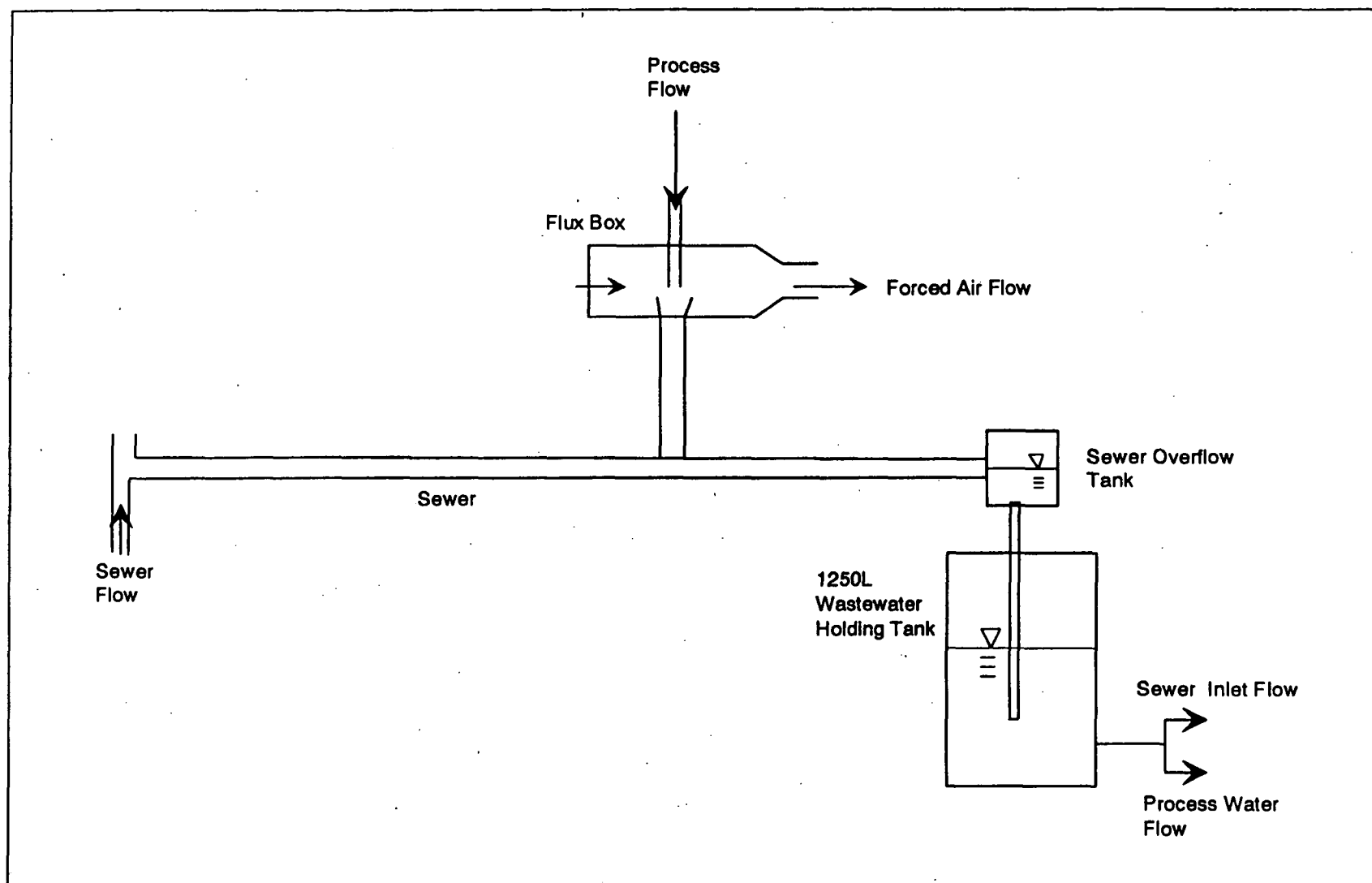


Figure II.2.1: Schematic of Apparatus

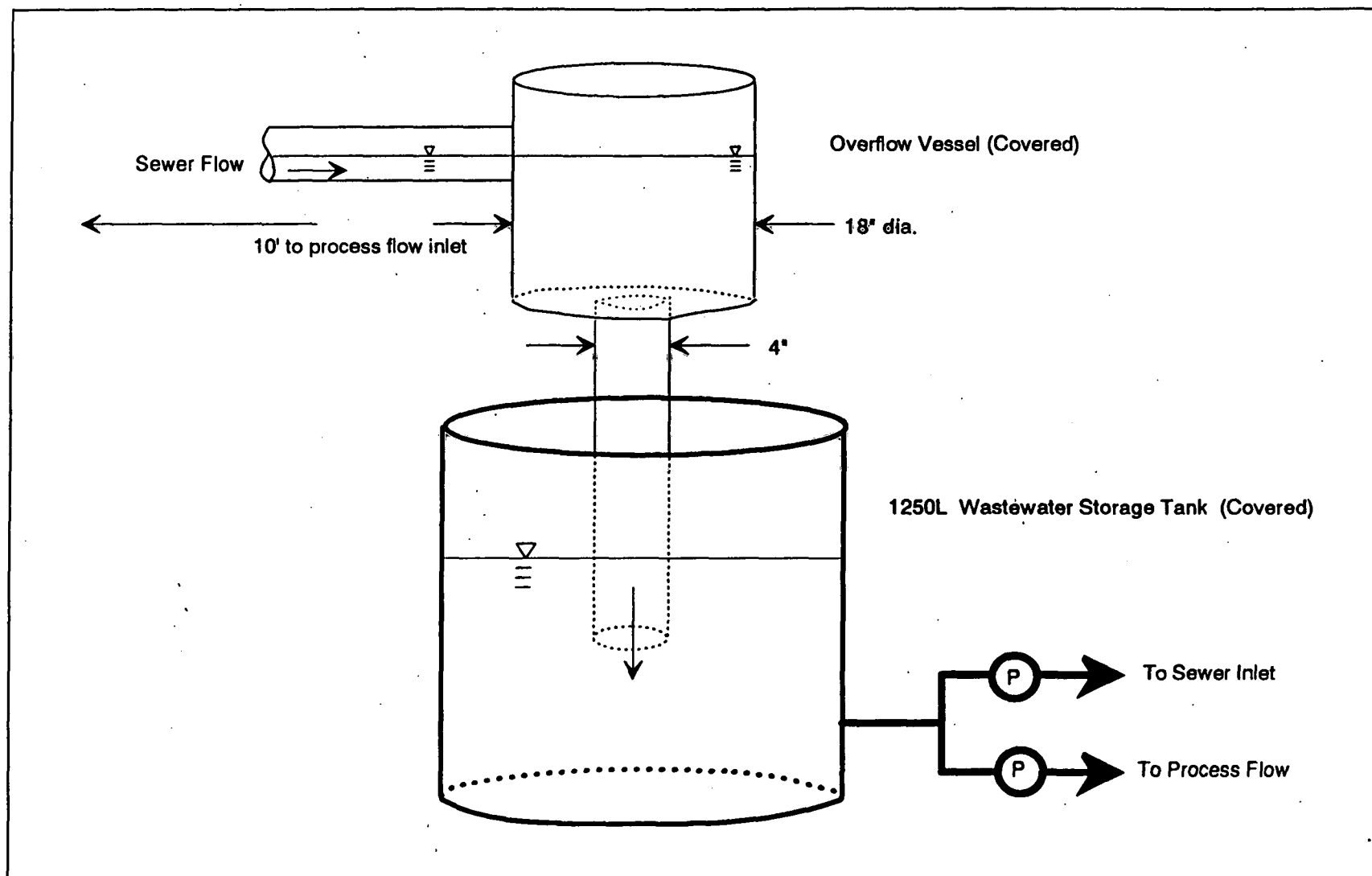


Figure II.2.2: Schematic of Sewer Outlet

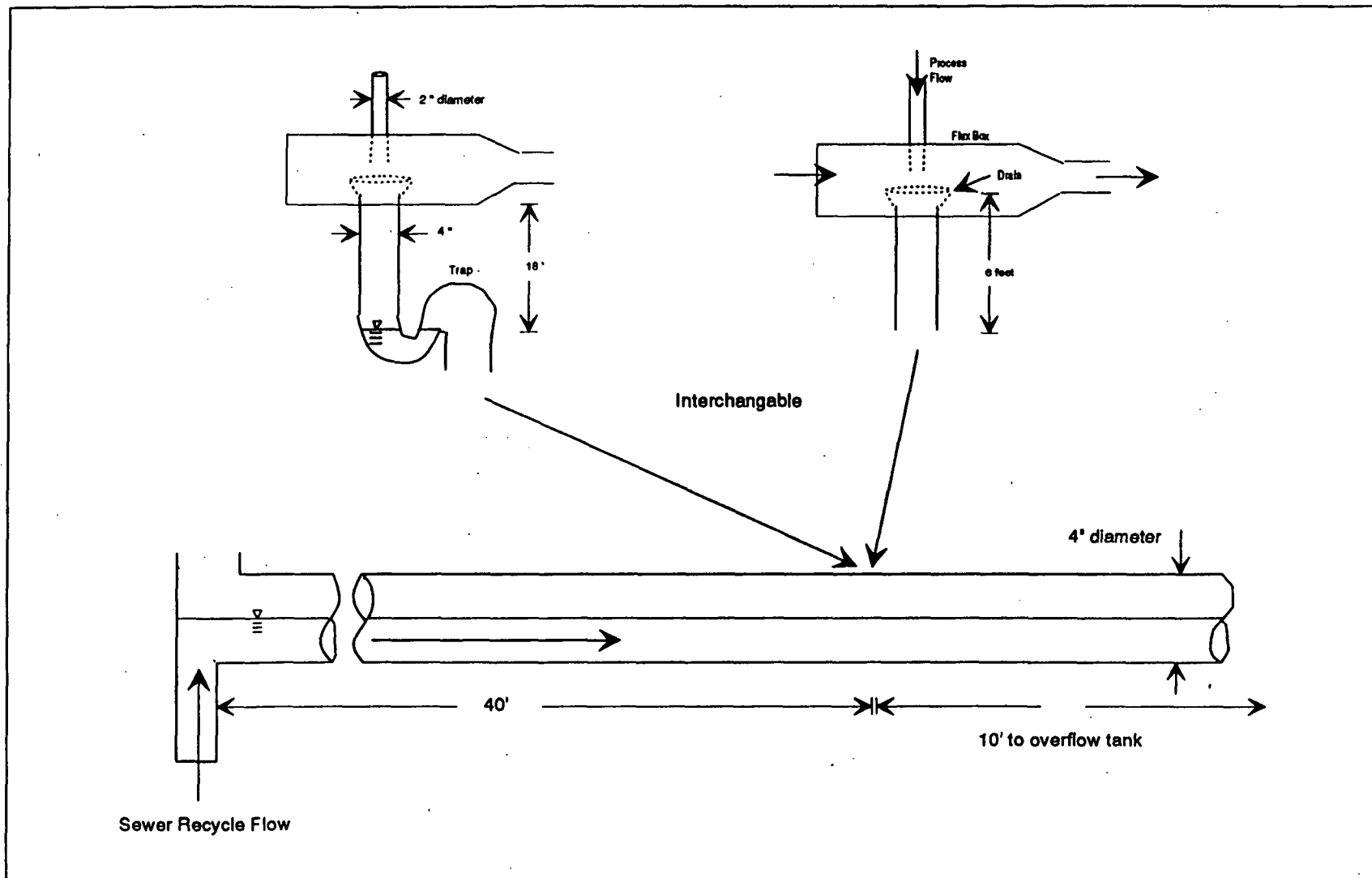


Figure II.2.3: Schematic of Drain Connection

II.2.1.2 SAMPLING AND ANALYTICAL METHODS

The wastewater consisted of tap water dosed with the five HAPs listed in Table II.2.1.

Table II.2.1: Summary of Analytical Methods					
Compound	H_{25} (m ³ /m ³)	Wastewater Analysis		Air Analysis	
		Method	MDL (ug/L)	Method	MDL (ng/L)
Tetrachloroethylene	0.71	EPA 1625	5 ug/L	EPA TO-14	10 ng/L
Trichloroethylene	0.41	EPA 1625	5 ug/L	EPA TO-14	10 ng/L
Toluene	0.26	EPA 1625	5 ug/L	EPA TO-14	10 ng/L
1,4 Dichlorobenzene	0.08	EPA 1625	5 ug/L	EPA TO-14	10 ng/L
Methanol	0.0006	GC-FID	5 mg/L	NIOSH 2000	5 ug/L

The first four compounds are generally regarded as volatile organic compounds (VOCs). Methanol has a much higher solubility and is generally regarded as a semi-volatile compound. All wastewater samples were collected in 60 mL amber, Teflon septum top bottles. Wastewater samples were taken by submerging the sample bottles at the sewer inlet, filling the bottle with no headspace. The four VOCs were analyzed using EPA Method 1625 and methanol was analyzed using direct aqueous injection into a gas chromatograph with an FID detector. Off-gas samples for VOC analysis were collected in 6.0 L stainless steel whole air sample canisters manufactured by Scientific Instrumentation Specialists (Moscow, Idaho) and analyzed using EPA Method TO-14. Off-gas samples for methanol analysis were collected by pulling 4 L of air through 5 cm long glass cartridges containing silica gel (35/70; mesh magnesium silicate) and analyzed using NIOSH Method 2000. References for all analytical methods are presented in Appendix II-A.

II.2.1.3 DOSING PROCEDURE

A stock solution containing the VOCs, dissolved in methanol, was prepared prior to dosing. To initiate dosing, the sewer flow was turned on, beginning the recycle of wastewater from the sewer to the storage tank. The stock solution was pumped, with a peristaltic pump, into the inlet of the sewer over a ten minute period. Thus, the dose compounds were continually carried along the length of the sewer and discharged into the storage tank over a ten minute period. This time represented approximately one hydraulic residence time of the wastewater storage tank. The sewer inlet was closed except for a small opening to allow for the pump tubing. The sewer flow was maintained for approximately 30 minutes after the end of the dose introduction, ensuring complete mixing of the dose compounds. The airflow through the flux box and the process water flow, if any, were turned on following the mixing period. Once the level in the sewer pipe had stabilized, the experiment was initiated with the collection of wastewater samples.

II.3 EXPERIMENTAL PLAN

Nine experiments, summarized in Table II.3.1, were completed. For the first two experiments, forced ventilation of the sewer line was carried out. Thus, the inlet to the flux box was sealed and air pulled from the sewer inlet, along the length of the sewer, up the straight pipe connection between the sewer and the drain, and out of the flux box. A constant ventilation rate of $12.2 \text{ m}^3/\text{d}$ was used for both experiments.

Seven experiments were carried out in which a wind over the drain was simulated. The wind velocity was 2 m/s (4.5 MPH) at the flux box inlet. For experiments 3-6, the connection between the drain and the sewer was made with the pipe with a P-trap. Experiment 4 was a repeat of experiment 3. For experiments 7-9, the connection between the drain and the sewer was made with a straight pipe. For both types of connections, experiments were carried out with a relatively low process water flowrate into the drain (10% of sewer inlet flow) and a relatively high process water flowrate into the drain (33% of process water flow).

The first two experiments were four hours in length, while remainder of the experiments were eight hours in length. Since there was a continual recycle of wastewater throughout each experiment, there was also a continuous reduction in the wastewater HAP concentration because of emissions (like a batch process). Thus, wastewater samples were collected at the beginning, mid-point and end of each experiment. Twenty three percent of the samples were collected in duplicate. Samples of the flux box exit gas were taken at the end of each experiment. For experiments air samples were also taken after four hours. Seventy percent of the gas samples were collected in duplicate. Background gas samples, consisting of the inlet air to the flux box, were collected during experiments 1, 5 and 8.

Table II.3.1 Experimental Operating Conditions

Expt. #	Ventilation	Drain Connection	Sewer Flow (L/min)	Process Water Flow (L/min)	Forced Ventilation Rate (m ³ /d)	Flux Box AirFlow Rate (m ³ /d)	Temperature (°C)	
							Liquid	Room Air
1	forced	straight	151	0	12.2		27	23
2	forced	straight	151	49	12.2		27	21
3	free	P-trap	170	0		28540	26	20
4	free	P-trap	170	0		28540	25	16
5	free	P-trap	151	15		28540	25	19
6	free	P-trap	151	49		28540	25	20
7	free	straight	170	0		28540	25	20
8	free	straight	151	15		28540	25	18
9	free	straight	151	49		28540	27	21

II.4 RESULTS AND DISCUSSION

II.4.1 VENTILATION RATE

The variables potentially inducing ventilation include:

- liquid drag
- wind eduction
- temperature differences between sewer and ambient atmosphere
- rise and fall of wastewater level

Flow of wastewater has the effect of entrainment of the overlying gas. Thus, without opposing factors, gas flow in sewers is generally in the same direction as the wastewater flow. Similarly, wastewater flowing into a drain through a sewer will tend to draw air into the sewer. Wind blowing over an opening between the sewer and atmosphere can cause a pressure difference between the sewer and atmosphere causing exhausting of the sewer gas. Temperature differences between the sewer air and atmosphere will induce airflow in the direction of declining temperature. A rise in the wastewater level will pump air out of the collection system and a fall in the wastewater level will pull air into the system.

While the potential variables affecting ventilation have been discussed qualitatively there is little information about actual ventilation rates observed in sewer pipes. Corsi¹ has estimated mean gas velocities caused by the individual ventilation mechanisms discussed above. However, the forces inducing ventilation may tend to induce airflow in opposite directions leading to a low net ventilation rate. It is generally thought that the ventilation rate increases as the number of openings between the sewer and the atmosphere increases. Openings must be present for both the inlet and outlet of air. Conversely, as the number and size of openings is decreased, the resistance to ventilation is increased.

A ventilation rate of 12.2 m³/day was selected for the ventilation rate during the forced ventilation experiments. This ventilation rate represents 100 turnovers/day of the empty sewer pipe or 200 turnovers/day of the half full sewer pipe. The corresponding velocity in the half full sewer pipe would be 0.035 m/s. It was thought that such a ventilation rate would be representative of actual ventilation rates in a system with many openings to the atmosphere. However, more experimental work is required to determine actual ventilation rates observed in full scale systems.

Headspace air velocities within the sewer pipe during the free ventilation experiments are presented in Table II.4.1. With a p-trap connection there was no detectable ventilation rate at the inlet of the sewer. There was a detection of air movement at mid-length in the sewer pipe. However, measurements were made using an anemometer which does not indicate ventilation direction. The detected airflow likely resulted from air swirling within the sewer pipe headspace.

With the straight pipe connection and no process water flow into the drain, an air velocity of 1.3 m/s was detected at the inlet of the sewer indicating that air was being pulled along the sewer by liquid drag and up the drain connection. This ventilation rate is extremely

high, but it should be understood that the liquid drag and wind eduction were both acting in the same direction and the flow in the pipe was relatively rapid (1 m/s). A contributing factor to the wind eduction was a 7 km/h differential between the drain and the sewer inlet. It does not represent a 7 km/h wind blowing over both openings. The air velocity within the sewer was substantially reduced with process water flow into the drain, indicating that the process flow tended to draw air into the drain countering the effects of liquid drag in the sewer and wind eduction.

Table II.4.1: Induced Air Velocity During Free Ventilation Experiments

Experiment No.	Process Flow	Flux Box Velocity (m/s)	Sewer Air Velocity At Inlet (m/s)	Sewer Air Velocity At Mid-length (m/s)
P-trap drain connection				
3	no	2.0	< 0.1	0.1 - 0.2
4	no	2.1	< 0.1	0.1
5	low	1.9	< 0.1	0.1 - 0.2
6	high	2.1	< 0.1	0.1 - 0.2
Straight drain connection				
7	no	2.0	1.3	
8	low	2.1	< 0.1	0.1 - 0.2
9	high	2.0	< 0.1	0.1 - 0.2

II.4.2 ANALYTICAL QUALITY ASSURANCE

A sample of room air was taken one hour before the initiation of experiment 1. Results are presented in Table II.4.2. The very low concentrations presented in Table 4.2 indicate no significant contamination of room air prior to an experiment. A sample of the flux box influent air was taken at the midpoint of experiments 4 and 5. Significant quantities of all VOCs were detected on these blank samples suggesting that there were emission points upstream of the flux box. Potential emission sources include the opening at the sewer inlet, pump leakages, storage tank leakages and miscellaneous connection leakages. As the wastewater descended from the sewer outlet into the storage tank it tended to entrain air. This entrained air would pressurize the air space of the storage tank increasing the leak likelihood. In addition, there may have been some re-circulation of flux box exhaust air although reasonable precautions were taken to minimize this.

Table II.4.3 presents results from the analysis of duplicate wastewater samples. The absolute difference of the duplicates was defined as the absolute value of the difference between the average and the measured concentrations. The relative difference was defined as the ratio of the absolute difference to the average measured concentration. For all samples the relative differences were less than 10%. Table II.4.4 presents results from the analysis of duplicate off-gas samples. The absolute and relative differences were defined as above. The relative difference between duplicate samples were consistently less than 25% and frequently less than 10%. Methanol was not detected in any off-gas samples.

Table II.4.2: Blank Gas Sample Analysis Results

Compound	Flux Box Influent Gas Concentration Before Experiment 1 (µg/L)	Flux Box Influent Gas Concentration During Experiment 4 (µg/L)	Flux Box Influent Gas Concentration During Experiment 5 (µg/L)
Methanol	< 5 E+0	< 5 E+0	< 5 E+0
1,4- Dichlorobenzene	< 1 E-2	4.0 E-3	2.9 E-2
Toluene	8 E-3	8.2 E-2	9.0 E-2
Trichloroethylene	2 E-2	2.2 E-1	1.7 E-1
Tetrachloroethylene	< 1 E-3	1.4 E-2	1.8 E-2

Table II.4.3: Comparison of Duplicate Wastewater Samples

Compound	Sample (mg/L)	Duplicate (mg/L)	Absolute Difference (mg/L)	Relative Difference (%)	Sample (mg/L)	Duplicate (mg/L)	Absolute Difference (mg/L)	Relative Difference (%)
	Experiment 1				Experiment 3			
Methanol	939	954	7.50	0.79	1008	1041	18.5	0.61
1,4-Dichlorobenzene	12.2	10.3	0.55	4.31	7.9	8.4	0.25	3.07
Toluene	180.5	210.8	11.65	5.78	52.5	57.2	2.35	4.28
Trichloroethylene	366.5	396.3	14.90	3.91	79.3	85.8	3.25	3.94
Tetrachloroethylene	25.9	27.8	0.95	3.54	7.2	8.0	0.40	5.26
	Experiment 6				Experiment 7			
Methanol	1112	1143	15.50	1.37	880	925	22.50	2.49
1,4-Dichlorobenzene	9.7	11.1	0.70	6.73	4.3	4.5	0.10	2.27
Toluene	56.1	63.6	3.75	6.27	27.0	27.4	0.20	0.74
Trichloroethylene	54.0	61.9	3.95	6.82	38.7	40.1	0.70	1.78
Tetrachloroethylene	2.7	3.3	0.30	10.00	3.6	3.9	0.15	4.00
	Experiment 8				Experiment 9			
Methanol								
1,4-Dichlorobenzene	5.4	5.7	0.15	2.70	1.6	1.7	0.05	3.03
Toluene	25.4	25.9	0.25	0.97	1.5	1.6	0.05	3.23
Trichloroethylene	19.1	19.4	0.15	0.78	0.6	0.6	0.00	0.00
Tetrachloroethylene	0.6	0.7	0.05	7.69	--	--	--	--
	Experiment 4							
Methanol	1321	1502	91	6.4				
	1499	1554	28	1.8				
	1380	1492	56	3.9				

Table II.4.4: Comparison of Duplicate Off-gas Samples

Compound	Sample (ug/L)	Duplicate (ug/L)	Absolute Difference (ug/L)	Relative Difference (%)	Sample (ug/L)	Duplicate (ug/L)	Absolute Difference (ug/L)	Relative Difference (%)
	Experiment 1				Experiment 2			
Methanol	< 5	< 5	--	--	< 5	< 5	--	--
1,4-Dichlorobenzene	8	7	0.5	1.3	525	507	9.0	1.7
Toluene	100	105	2.5	2.4	3880	3600	140.0	3.7
Trichloroethylene	347	373	13.0	3.6	17800	13800	2000.0	12.7
Tetrachloroethylene	48	48	0.0	0.0	783	695	49.0	6.6
	Experiment 3				Experiment 4			
Methanol	< 5	< 5	--	--	< 5	< 5	--	--
1,4-Dichlorobenzene	.011	.015	0.002	15.4	2.4	2.4	0.0	--
Toluene	.104	.093	0.006	5.6	17.1	18.1	0.5	2.8
Trichloroethylene	.283	.367	0.042	12.9	44.6	57.2	8.3	12.4
Tetrachloroethylene	.048	.038	0.004	9.5	3.9	3.8	0.1	1.3
	Experiment 7				Experiment 8			
Methanol	< 5	< 5	--	--	< 5	< 5	--	--
1,4-Dichlorobenzene	3.1	2.7	0.2	6.9	1.3	1.1	0.1	8.4
Toluene	18.6	14.4	1.1	7.1	10.6	13.9	1.7	13.5
Trichloroethylene	50.3	43.2	3.6	7.6	30.6	50.4	9.9	24.4
Tetrachloroethylene	3.4	3.0	0.2	6.3	0.9	0.6	0.1	1.1
	Experiment 9							
Methanol	< 5	< 5	--	--				
1,4-Dichlorobenzene	.55	.61	0.03	5.2				
Toluene	1.68	1.30	0.29	18.2				
Trichloroethylene	1.08	1.55	0.24	17.9				
Tetrachloroethylene	0.13	0.09	0.02	16.2				

II.4.3 EMISSION RATES

II.4.3.1 FORCED VENTILATION EXPERIMENTS

Summaries of the raw data collected during the two forced ventilation experiments are presented in Tables II.4.5 and II.4.6. There was no process water flow into the drain during the first experiment. The process water flowrate into the drain during the second experiment was 33% of the sewer influent flowrate. Since there was a continual recycle of wastewater throughout the experiments, a decline in wastewater HAP concentration is expected if there were significant emissions (like a batch process). For the first experiment, there was no decline in the wastewater concentration of any VOC or methanol. For the second experiment, the wastewater concentration of toluene, trichloroethylene and tetrachloroethylene decreased, while the wastewater concentration of methanol and 1,4 dichlorobenzene were relatively constant. The flux box effluent gas concentration of the four VOCs were an order of magnitude higher in the second experiment than they were in the first experiment. This indicates that the process water flow into the drain significantly increased VOC emissions from the drain. The increased emissions were likely caused by stripping of the VOCs as the process flow into the drain proceeded downwards, concurrent to the air flow, and due to splashing as the process water dropped into the sewer. The splashing would increase turbulence and thus mass transfer. Methanol was not detected in any off-gas sample.

Table II.4.5: Raw Data Summary - Experiment 1

Operating Conditions	Process Connection		Sewer Flowrate (L/min)		Process Water Flowrate (L/min)	
	straight		151		0	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)	
	t = 0	t = 2 h	t = 4 h	t = 4 h	t = 4 h	t = 4 h
Methanol	998.0	-	954.0	939.0	< 5.0	< 5.0
1,4-Dichlorobenzene	11.9	12.8	12.2	13.3	7.6	7.4
Toluene	189.7	184.0	190.5	213.8	100.0	105.0
Trichloroethylene	341.8	316.0	366.5	396.3	347.0	373.0
Tetrachloroethylene	26.7	27.2	25.9	27.8	46.0	46.0

Table II.4.6: Raw Data Summary - Experiment 2

Operating Conditions	Process Connection		Sewer Flowrate (L/min)	Process Water Flowrate (L/min)	
	straight		151	49	
Compounds	Liquid Concentration (mg/L)			Gas Concentration (µg/L)	
	t = 0	t = 2 h	t = 4 h	t = 4 h	t = 4 h
Methanol	956.0	-	959.0	< 5.0	< 5.0
1,4-Dichlorobenzene	10.7	14.6	11.8	525	507.0
Toluene	137.9	134.5	95.1	3880	3600
Trichloroethylene	215.5	181.5	111.1	17800	13800
Tetrachloroethylene	13.9	16.4	6.3	793	695

Table II.4.7 summarizes the HAP emission rates calculated for the two forced ventilation experiments. The first numerical column, E_G presents the emission rate based upon the flux box effluent gas concentration at time $T = 4$ hours. E_G was calculated by multiplying the measured gas concentrations by the measured ventilation rate. The second and third numerical columns, $E_{G,rel1}$ and $E_{G,rel2}$ represent the percentage ratio of E_G to the initial and final wastewater mass flowrates of each HAP. For example, the initial wastewater mass flowrate [g/d] was calculated by multiplying the initial wastewater concentration [g/L] by the sum of the sewer and process water flowrates [L/d]. Similarly, the final wastewater mass flowrate was calculated by multiplying the final wastewater concentration by the sum of the sewer and process water flowrates. $E_{G,rel}$ represents the instantaneous emission rate expressed as a percentage of the instantaneous mass flowrate of each HAP flowing in the sewer downstream of the drain connection. Under steady state conditions, $E_{G,rel}$ would be a constant value. However, in these experiments, wastewater was continually recycled resulting in a decrease in wastewater HAP concentration over time due to emissions (like a batch process). Therefore $E_{G,rel}$ was calculated as a fraction of the wastewater mass flows at the beginning of the experiment ($E_{G,rel,1}$) and end of experiment ($E_{G,rel,2}$). The instantaneous $E_{G,rel}$ would be within this range.

For the first experiment, the emission rates of all HAPs were less than .01% of the wastewater mass flowrate. Since methanol was not detected in the gas samples, the maximum emission rate was calculated using the method detection limit for the analysis. For the second experiment, the emission rates of all HAPs were less than 1% of the wastewater mass flowrate. Thus, the process flow into the drain significantly increased emissions although they remained a small percentage of the wastewater mass flowrate.

Table II.4.7: Emission Rate Summary Forced Ventilation Experiments

Compound	E_G [T=4 h] (g/day)	$E_{G,rel1}$ (% of initial liquid mass flowrate)	$E_{G,rel2}$ (% of final liquid mass flowrate)
Experiment Number 1 (no process flow)			
Methanol	< 6.1 E-2	< 3.0 E -5	< 3.0 E -5
1,4-Dichlorobenzene	9.2 E-2	3.5 E -3	3.3 E -3
Toluene	1.3 E+0	3.0 E -3	2.8 E -3
Trichloroethylene	4.4 E+0	5.9 E -3	5.3 E -3
Tetrachloroethylene	5.6 E-1	9.7 E -3	9.6 E -3
Experiment Number 2 (high process flow)			
Methanol	< 6.1 E-2	< 2.0 E-5	< 2.0 E-5
1,4-Dichlorobenzene	6.3 E+0	2.0 E-1	1.9 E-1
Toluene	4.6 E+1	1.1 E-1	1.7 E-1
Trichloroethylene	1.9 E+2	3.1 E-1	6.0 E-1
Tetrachloroethylene	9.1 E+0	2.3 E-1	5.0 E-1

II.4.3.2 FREE VENTILATION EXPERIMENTS: P-trap Connection

Summaries of the raw data collected during the four free ventilation experiments with a P-trap drain connection are presented in Tables II.4.8 to II.4.11. Experiment 4 (Table 4.9) was a repeat of experiment 3 (Table II.4.8). As explained in Section II.4.3.1, because wastewater was recycled throughout the experiments, a decline in wastewater HAP concentration was expected if there were significant HAP emissions (like a batch process). For experiment 3 and 4 there was a decline in the wastewater concentration of all VOCs. There was no decline in the methanol wastewater concentration. In experiments 5 and 6, with process water flow into the drain, there were greater relative declines in wastewater VOC concentration and higher flux box effluent gas concentrations, indicating greater emissions. The greater emissions were likely caused by three potential mechanisms:

- splash increasing turbulence
- potential countercurrent flow of air and process water in drain connection
- stripping caused by wind blowing around free falling liquid above drain

Table II.4.8: Raw Data Summary - Experiment 3

Operating Conditions	Process Connection		Sewer Flowrate (L/min)		Process Water Flowrate (L/min)	
	P-trap		170		0	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)	
	t=0	t=0 h	t=8 h	t=8 h	t=8 h	t=8 h
Methanol	976	-	1008	1041	< 5.0	< 5.0
1,4-Dichlorobenzene	9.28	9.4	7.94	8.35	0.011	0.015
Toluene	68.5	69.3	52.5	57.2	0.104	0.093
Trichloroethylene	113.0	114.0	79.3	85.8	0.283	0.367
Tetrachloroethylene	12.4	13.1	7.23	8.0	0.046	0.038

Table II.4.9: Raw Data Summary - Experiment 4

Operating Conditions	Process Connection		Sewer Flowrate (L/min)	Process Water Flowrate (L/min)	
	P-trap		170	0	
Compounds	Liquid Concentration (mg/L)			Gas Concentration (µg/L)	
	t=0	t=4h	t=8h	t=4h	t=8h
Methanol	1502, 1321	1554, 1499	1492, 1380	< 5.0	< 5.0
1,4-Dichlorobenzene	12.4	11.4	9.99	0.007	0.008
Toluene	106.0	100.0	87.9	0.089	0.066
Trichloroethylene	130.0	114.0	100.5	0.220	0.138
Tetrachloroethylene	12.8	10.1	8.0	0.014	0.010

Table II.4.10: Raw Data Summary - Experiment 5

Operating Conditions	Process Connection		Sewer Flowrate (L/min)	Process Water Flowrate (L/min)	
	P-trap			151	15
Compounds	Liquid Concentration (mg/L)				
	t=0	t=4h	t=8h	t=4h	t=8h
Methanol	807	931	891	< 5.0	< 5.0
1,4-Dichlorobenzene	6.42	4.52	3.01	1.01	0.59
Toluene	65.5	32.3	17.2	6.14	2.81
Trichloroethylene	89.4	37.6	18.2	14.72	7.18
Tetrachloroethylene	7.58	2.94	1.13	1.34	0.44

Table II.4.11: Raw Data Summary - Experiment 6

Operating Conditions	Process Connection		Sewer Flowrate (L/min)		Process Water Flowrate (L/min)	
	P-trap		151		49	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)	
	t=0	t=4 h	t=4 h	t=8 h	t=4 h	t=4 h
Methanol	1007	1095	-	1128	< 5.0	< 5.0
1,4-Dichlorobenzene	14.9	9.66	11.08	6.61	2.39	2.44
Toluene	155.0	56.1	63.6	24.90	17.06	18.08
Trichloroethylene	225.0	54.0	61.9	18.60	44.60	57.16
Tetrachloroethylene	20.1	2.7	3.33	0.71	3.91	3.78

Since the wastewater concentration of the contaminants declined substantially during the experiments, steady state assumptions were assumed to be invalid. Therefore, dynamic modelling of the decline in wastewater concentration was chosen to represent the system.

A first order rate of decline in wastewater concentration can be expressed as:

$$\frac{dC_L}{dt} = -k_L C_L \quad (1)$$

where C_L is the wastewater concentration and k_L is the effective mass transfer coefficient for the system. The effective mass transfer coefficient lumps all transfer mechanisms and would change as operating conditions change. Integrating this equation from time 0 to time t provides the following equation:

$$C_L = C_{L0} \exp(-k_L * t) \quad (2)$$

This can also be expressed in the following form:

$$\ln C_L = \ln C_{L0} - k_L * t \quad (3)$$

The negative slope of a linear plot of $\ln C_L$ versus T represents the effective mass transfer coefficient based on liquid concentration.

Figures II.4.1 to II.4.4 are plots of the wastewater concentrations observed during experiments 3 to 6. The x-axis scale of the plot is linear. The y-axis scale of the plot is natural logarithmic. Included on the plots are linearly regressed lines and R^2 value. For experiments 3 and 4, the k_L values ranged from 0.02 h^{-1} to 0.07 h^{-1} and generally increased with increasing compound volatility. The R^2 values were consistently greater than 0.9. For experiment 5, the K_L values ranged from 0.1 to 0.2 h^{-1} and also increased with compound volatility. These values were approximately one order of magnitude greater than experiment 3 and 4 suggesting that the process flow into the drain significantly increased mass transfer. For experiment 6, the K_L values were greater than those observed in experiment 5, but by a factor less than 2. Thus, the increased process water flow increased mass transfer but not dramatically.

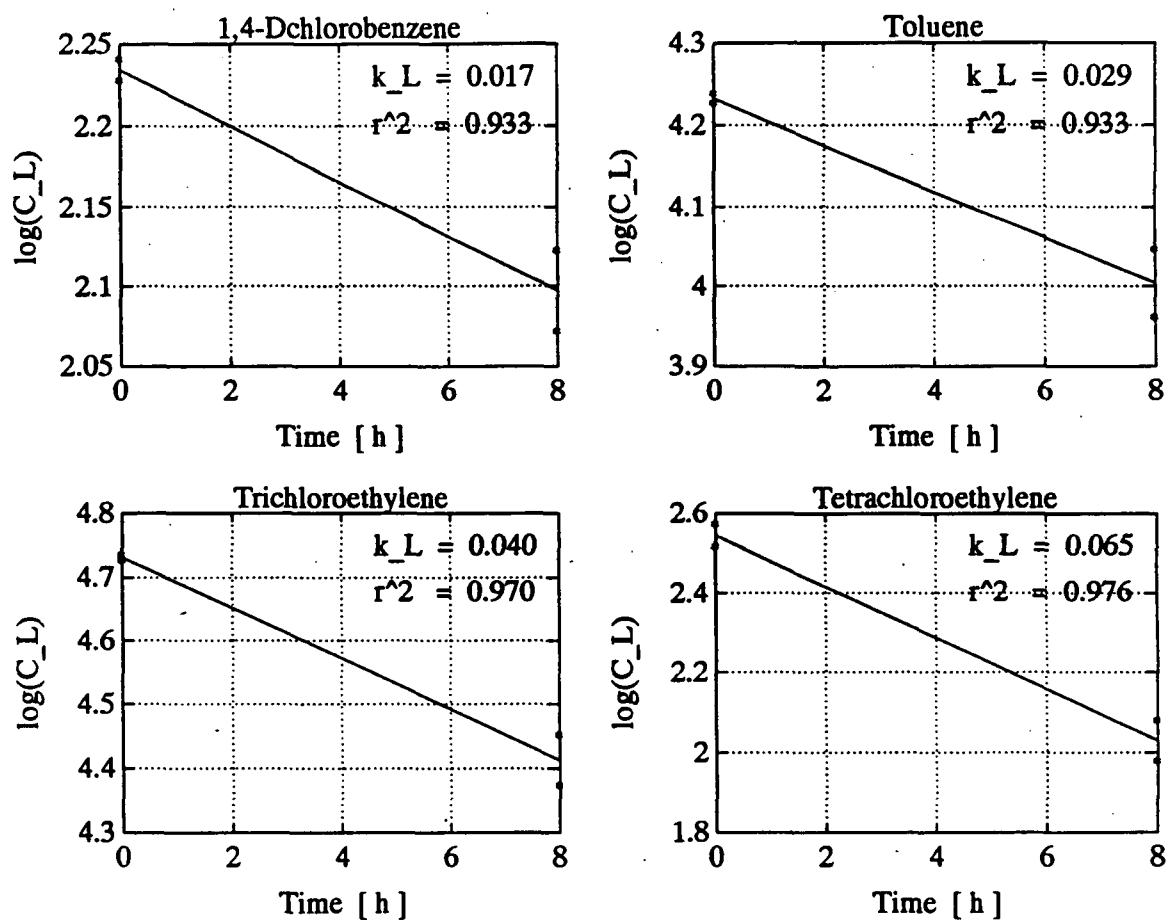


Figure II.4.1: Experiment 3: Plot of $\ln C_L$ vs Time

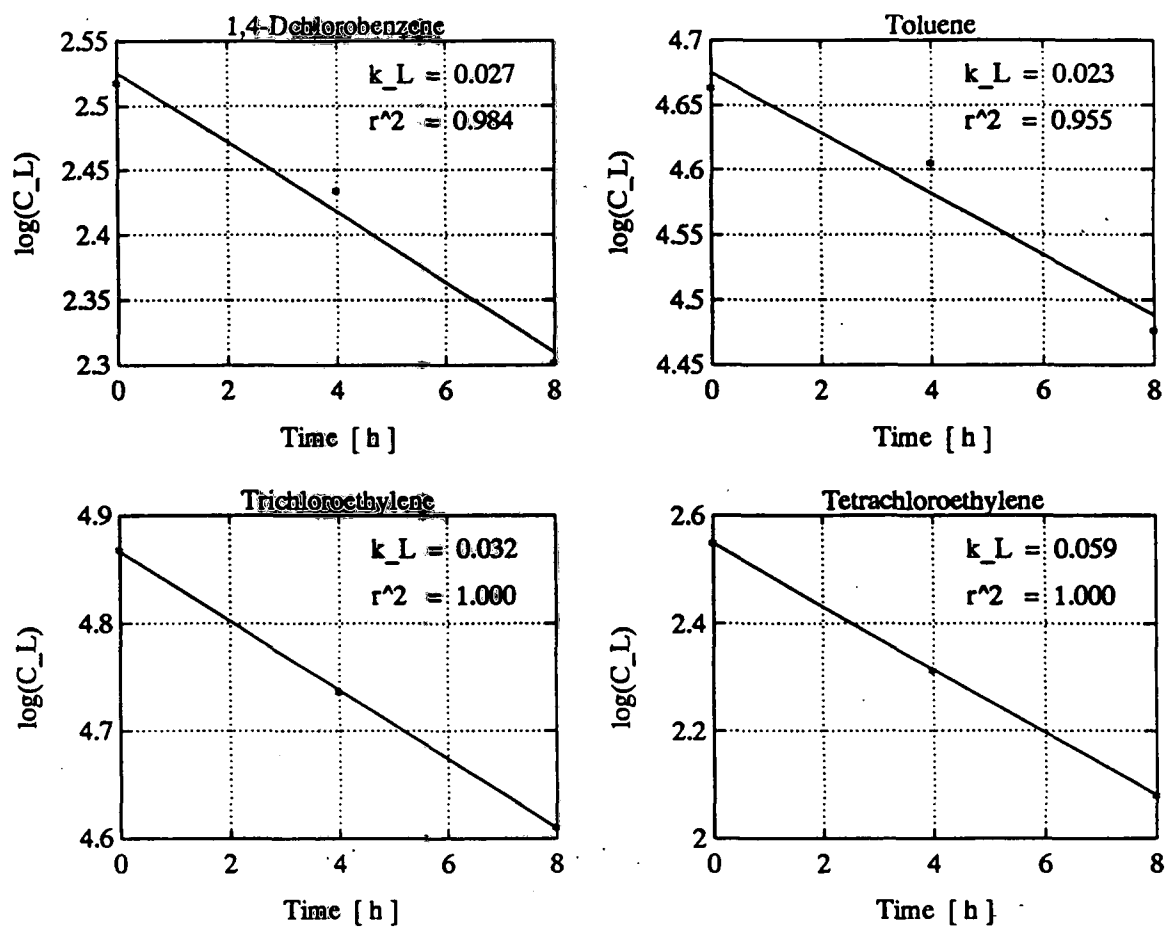


Figure II.4.2 Experiment 4 - Plot of $\ln C_L$ vs Time

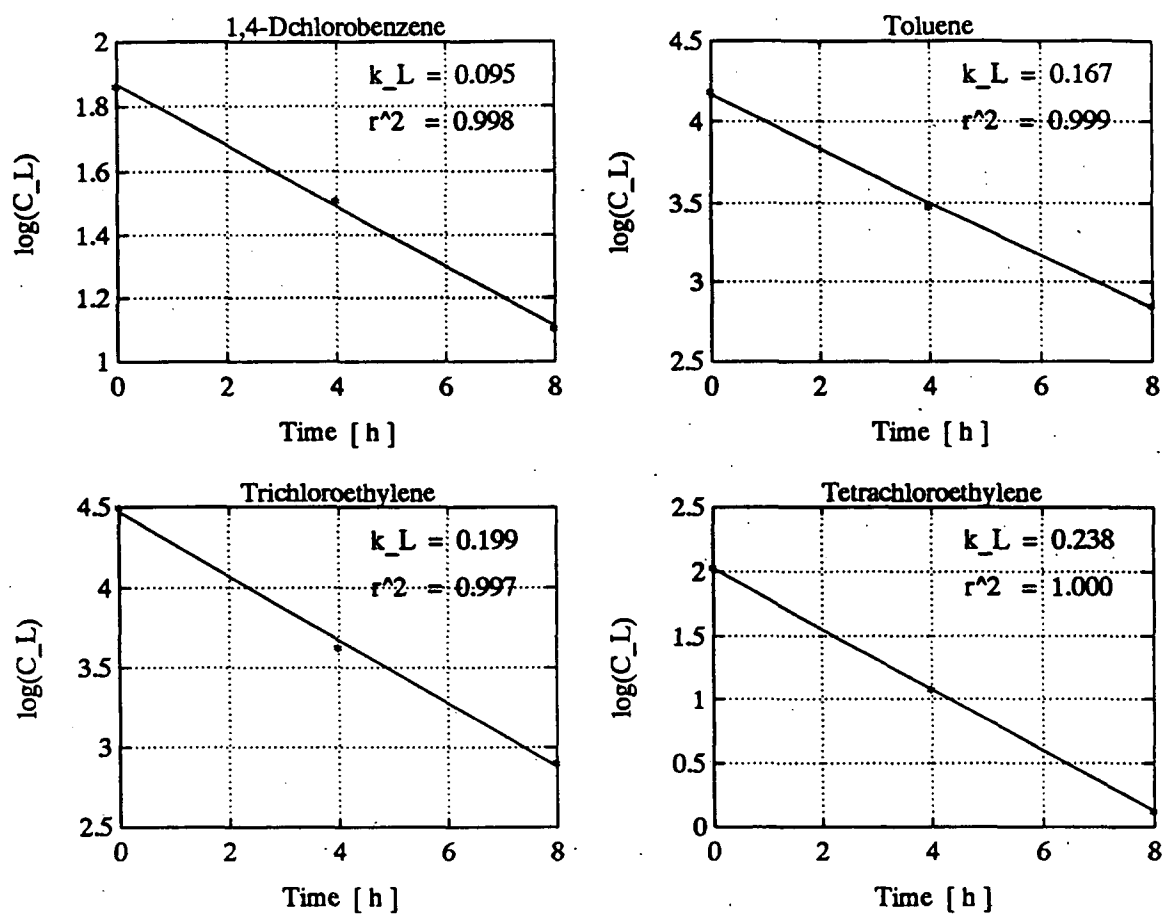


Figure II.4.3: Experiment 5 - Plot of $\ln C_L$ vs Time

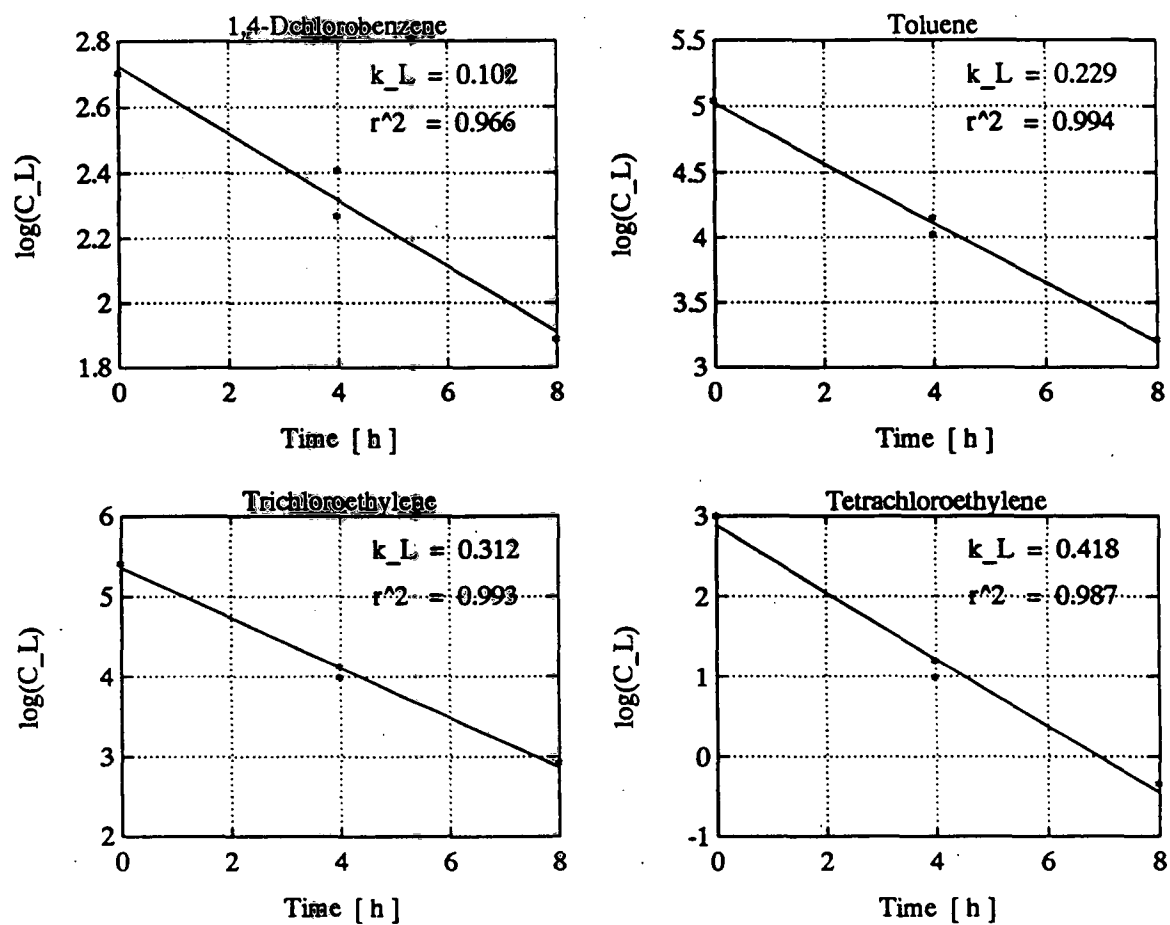


Figure II.4.4 Experiment 6 - Plot of $\ln C_L$ vs Time

The emission rate summary for the free ventilation experiments with a P-trap drain connection is presented in Table II.4.11. The first numerical column E_L in Table II.4.11 represents the average emission rate over the length of the experiment based upon the observed losses in the wastewater concentration. The second and third numerical columns, $E_{L,rel1}$ and $E_{L,rel2}$ represent the percentage ratio of E_L to the initial and final wastewater mass flowrates of each HAP. For example, the initial wastewater mass flowrate [g/d] was calculated by multiplying the initial wastewater concentration [g/L] by the sum of the sewer and process water flowrates [L/d]. Similarly, the final wastewater mass flowrate was calculated by multiplying the final wastewater concentration by the sum of the sewer and process water flowrates. $E_{L,rel}$ represents the instantaneous emission rate expressed as a percentage of the instantaneous mass flowrate of each HAP flowing in the sewer downstream of the drain connection. Under steady state conditions, $E_{L,rel}$ would be a constant value. However, in these experiments, wastewater was continually recycled resulting in a decrease in wastewater HAP concentration over time due to emissions (like a batch process). Therefore $E_{L,rel}$ was calculated as a fraction of the wastewater mass flows at the beginning of the experiment ($E_{L,rel,1}$) and end of experiment ($E_{L,rel,2}$). The instantaneous $E_{L,rel}$ would be within this range.

The fourth and seventh numerical columns, E_G present the emission rates based upon the flux box effluent gas concentrations at time $T = 4$ hours and time $T = 8$ hours. E_G was calculated by multiplying the measured flux box effluent gas concentration by the flux box effluent air flowrate. E_G should be related to the wastewater concentration. As the wastewater concentration declines, E_G also will decline. However, there will be a lag between liquid and gas phase concentrations due to mass transfer effects. Numerical columns 5,6 and 7,8 ($E_{G,rel}$) represent the percentage ratio of E_G to the initial and final wastewater mass flowrates of each HAP. Columns 5 and 6 are based upon the gas measurement at $T = 4$ hours and columns 7 and 8 are based upon the gas measurement at time $T = 8$ hours.

Methanol was not detected in the flux box effluent gas during any of the four experiments. Thus, the maximum E_G and $E_{G,rel}$ were calculated based upon the gas measurement method detection limit. There was not a consistent decline in the methanol wastewater concentration over the experiments and E_L could not be calculated.

For experiments 3 and 4, the relative emission rate of the VOCs based upon wastewater concentration ranged from 0.2% to 1%. The relative emission rate of the VOCs based upon the flux box effluent gas phase concentration measurements ranged from 0.01% to 0.06%. These values were not corrected for the VOC concentrations observed in the flux box influent gas. Thus, these measurements may overestimate actual emissions from the drain. The emission measurements based upon the decline in wastewater concentration were significantly higher than those based upon flux box effluent gas concentration measurements. The emission measurements based on the decline in wastewater concentration account for all emission sources including leaks. The gas phase measurements account only for emissions from the drain. Thus, when emissions from miscellaneous leaks are a significant percentage of total emissions, the emission measurements based on the decline in wastewater VOC concentration will overestimate drain emissions.

For experiment 5, the emission rates of the VOCs, based upon flux box effluent gas concentrations were significantly greater at time $T = 4$ than $T = 8$ indicating that the emission rate decreased as the wastewater concentration decreased. For both experiments 5 and 6, the average emission rates, calculated from the wastewater concentrations, were the same order of magnitude as the emission rates calculated from the gas measurements. This indicates that both measurement methods were comparable when emissions from miscellaneous leaks were a small percentage of drain emissions.

For experiments 5 and 6, the relative emission rates of the VOCs, expressed as a percentage of the final wastewater concentration, were significantly higher than those expressed as a percentage of the initial wastewater concentration because of the significant decline in wastewater concentration over the length of the experiment. The values expressed as a percentage of the initial and final wastewater concentrations represent the range of relative emissions. The actual relative emission rate should fall within this range. Based upon initial wastewater concentration, the lowest relative emission rate was 0.51% for toluene and the highest was 2.24% for trichloroethylene. Based upon final wastewater concentration, the lowest relative emission rate was 1.95% for toluene and 53.7% for tetrachloroethylene.

Table II.4.11: Emission Rate Summary - Free Ventilation With P-Trap Drain Connection

Compound	E_L (g/d)	E_{L1} (% of initial liquid mass flowrate)	E_{L2} (% of final liquid mass flowrate)	E_G [T = 4 h] (g/day)	E_{G1} (% of initial liquid mass flowrate)	E_{G2} (% of final liquid mass flowrate)	E_G [T = 8 h] (g/day)	E_{G1} (% of initial liquid mass flowrate)	E_{G2} (% of final liquid mass flowrate)
Experiment Number 3 (no process flow)									
Methanol							< 1.7 E+2	< 6.9 E-2	< 6.5 E-2
1,4-Dichlorobenzene	4.5 E+0	2.0 E-1	2.3 E-1				3.7 E-1	1.6 E-2	1.9 E-2
Toluene	5.3 E+1	3.1 E-1	3.4 E-1				2.8 E+0	1.7 E-2	2.1 E-2
Trichloroethylene	1.2 E+2	4.2 E-1	5.8 E-1				9.3 E+0	3.3 E-2	4.6 E-2
Tetrachloroethylene	1.9 E+1	6.2 E-1	1.0 E+0				1.2 E+0	3.8 E-2	6.4 E-2
Experiment Number 4 (no process flow)									
Methanol							1.4 E+2	< 3.9 E-2	< 3.8 E-2
1,4-Dichlorobenzene	9.0 E+0	3.0 E-1	3.7 E-1	2.1 E-1	7.0 E-3	8.0 E-3	2.2 E-1	7.0 E-3	9.0 E-3
Toluene	6.8 E+1	2.6 E-1	3.2 E-1	2.5 E+0	1.0 E-2	1.2 E-2	1.9 E+0	7.0 E-3	9.0 E-3
Trichloroethylene	1.1 E+2	3.5 E-1	4.5 E-1	6.3 E+0	2.0 E-2	2.6 E-2	3.9 E+0	1.2 E-2	1.6 E-2
Tetrachloroethylene	1.8 E+1	5.7 E-1	9.2 E-1	4.1 E-1	1.3 E-2	2.1 E-2	2.8 E-1	9.0 E-3	1.4 E-2

Table II.4.11 Cont'd: Emission Rate Summary - Free Ventilation With P-trap Drain Connection

Compound	E_L (g/d)	E_{L1} (% of initial liquid mass flowrate)	E_{L2} (% of final liquid mass flowrate)	E_G [T = 4 h] (g/day)	E_{G1} (% of initial liquid mass flowrate)	E_{G2} (% of final liquid mass flowrate)	E_G [T = 8 h] (g/day)	E_{G1} (% of initial liquid mass flowrate)	E_{G2} (% of final liquid mass flowrate)
Experiment Number 5 (low process flow)									
Methanol				< 1.4 E+2	< 7.5 E-2	< 6.8 E-2	< 1.4 E+2	< 7.5 E-2	< 6.8 E-2
1,4-Dichlorobenzene	1.3 E+1	8.3 E-1	1.8 E+0	2.9 E+1	1.9 E+0	4.0 E+0	1.7 E+1	1.1 E+0	2.3 E+0
Toluene	1.8 E+2	1.2 E+0	4.4 E+0	1.8 E+2	1.1 E+0	4.3 E+0	8.0 E+1	5.1 E-1	2.0 E+0
Trichloroethylene	2.7 E+2	1.3 E+0	6.1 E+0	4.2 E+2	2.0 E+0	9.7 E+0	2.0 E+2	9.6 E-1	4.7 E+0
Tetrachloroethylene	2.4 E+1	1.3 E+0	9.0 E+0	3.8 E+1	2.1 E+0	1.4 E+1	1.3 E+1	6.9 E-1	4.7 E+0
Experiment Number 6 (high process flow)									
Methanol				< 1.4 E+2	< 4.9 E-2	< 4.4 E-2			
1,4-Dichlorobenzene	3.1 E+1	7.2 E-1	1.6 E+0	6.9 E+1	1.6 E+0	3.6 E+0			
Toluene	4.9 E+2	1.1 E+0	6.8 E+0	5.0 E+2	1.1 E+0	7.0 E+0			
Trichloroethylene	7.7 E+2	1.2 E+0	1.5 E+1	1.5 E+3	2.2 E+0	2.7 E+1			
Tetrachloroethylene	7.2 E+1	1.3 E+0	3.6 E+1	1.1 E+2	1.9 E+0	5.4 E+1			

II.4.3.3 FREE VENTILATION EXPERIMENTS: Straight Pipe Connection

Summaries of the raw data collected during the three free ventilation experiments with a straight drain connection are presented in Tables II.4.12 to II.4.14. As explained in Section II.4.3.1, because wastewater was recycled throughout each experiment, a decline in wastewater HAP concentration was expected if there were significant HAP emissions (like a batch process). For all experiments there was a decline in the wastewater concentration of all VOCs. There was no consistent decline in the methanol wastewater concentration.

Table 4.12: Raw Data Summary - Experiment 7

Operating Conditions	Process Connection		Sewer Flowrate (L/min)		Process Water Flowrate (L/min)	
	straight		170		0	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)	
	t=0	t=4 h	t=8 h	t=8 h	t=8 h	t=8 h
Methanol	961	-	880	925	< 5.0	< 5.0
1,4-Dichlorobenzene	11.2	8.66	4.32	4.46	3.1	2.7
Toluene	189.0	70.2	27.0	27.4	16.6	14.4
Trichloroethylene	351.0	104.0	38.7	40.1	50.3	43.2
Tetrachloroethylene	25.0	9.86	3.63	3.92	3.4	3.0

Table II.4.13: Raw Data Summary - Experiment 8

Operating Conditions	Process Connection		Sewer Flowrate (L/min)		Process Water Flowrate (L/min)	
	straight		151		15	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)	
	t=0	t=4 h	t=4 h	t=8 h	t=4 h	t=4 h
Methanol	1484	1562	-	1364	< 5.0	< 5.0
1,4-Dichlorobenzene	10.4	5.45	5.67	3.22	1.29	1.09
Toluene	82.1	25.4	25.9	10.4	10.6	13.9
Trichloroethylene	85.8	19.1	19.4	6.57	30.6	50.4
Tetrachloroethylene	6.46	0.62	0.67	0.14	0.85	0.83

Table II.4.14: Raw Data Summary - Experiment 9

Operating Conditions	Process Connection	Sewer Flowrate (L/min)				Process Water Flowrate (L/min)	
	straight	151				49	
Compounds	Liquid Concentration (mg/L)				Gas Concentration (µg/L)		
	t=0	t=4 h	t=8 h	t=8 h	t=4 h	t=4 h	
Methanol	1046	1120	943	968	< 5.0	< 5.0	
1,4-Dichlorobenzene	7.35	3.18	1.60	1.66	0.55	0.61	
Toluene	30.3	5.78	1.49	1.56	1.88	1.30	
Trichloroethylene	27.1	2.64	0.56	0.62	1.08	1.55	
Tetrachloroethylene	2.44				0.13	0.09	

Figures II.4.5 to II.4.7 are plots of the wastewater concentrations observed during experiments 7 to 9. The plots have the same format as those discussed in Section II.4.3.2. For experiment 7, with no process water flow into the drain, the K_L values ranged from 0.1 h^{-1} to 0.3 h^{-1} . K_L values generally increased by a factor ranging from 1.25 to 1.75 in experiment 8, with a process water flowrate into the drain 10% of the sewer influent flowrate. K_L values increased further in experiment 9, with a process water flowrate into the drain 33% of the sewer influent flowrate. Thus, as discussed in Section II.4.3.2 the presence of process water flow into the drain increased the effective mass transfer coefficient. However, the increase in mass transfer coefficient from the conditions of no process water flow to the condition of process flow into the process drain was less severe than the case where the drain connection had a P-trap. Thus, it is postulated that without the P-trap, significant mass transfer resulted from air that was drawn through the sewer pipe and up the straight drain connection.

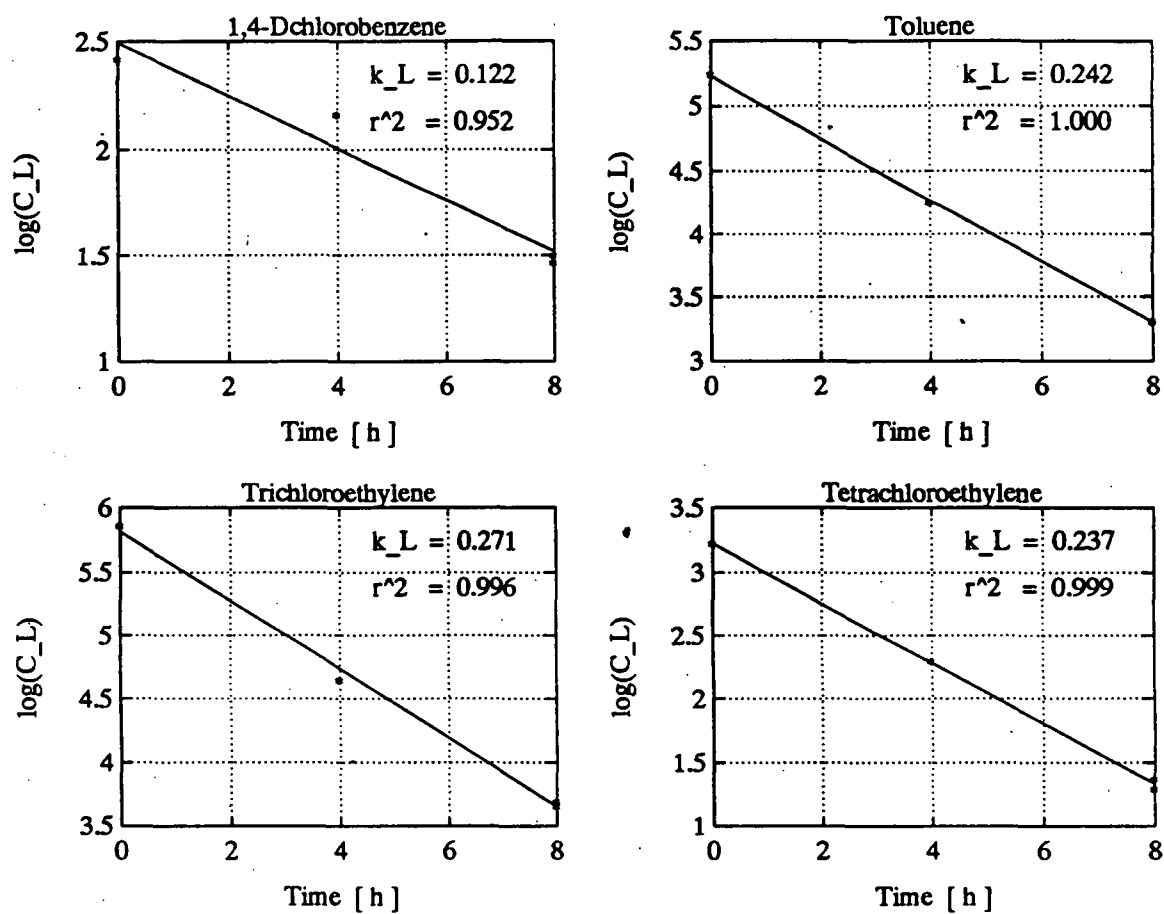


Figure II.4.5 Experiment 7 - Plot of $\ln C_L$ vs Time

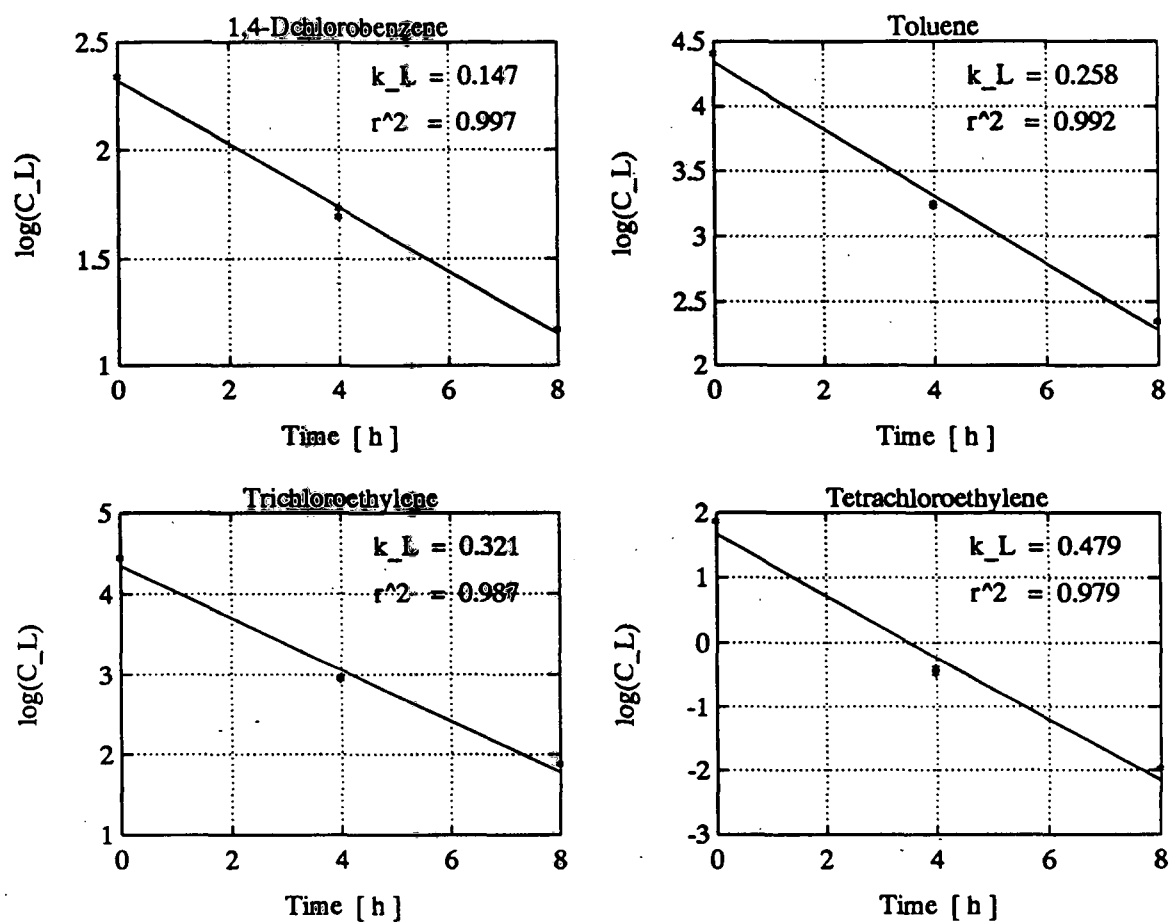


Figure II.4.6 Experiment 8 - Plot of $\ln C_L$ vs Time

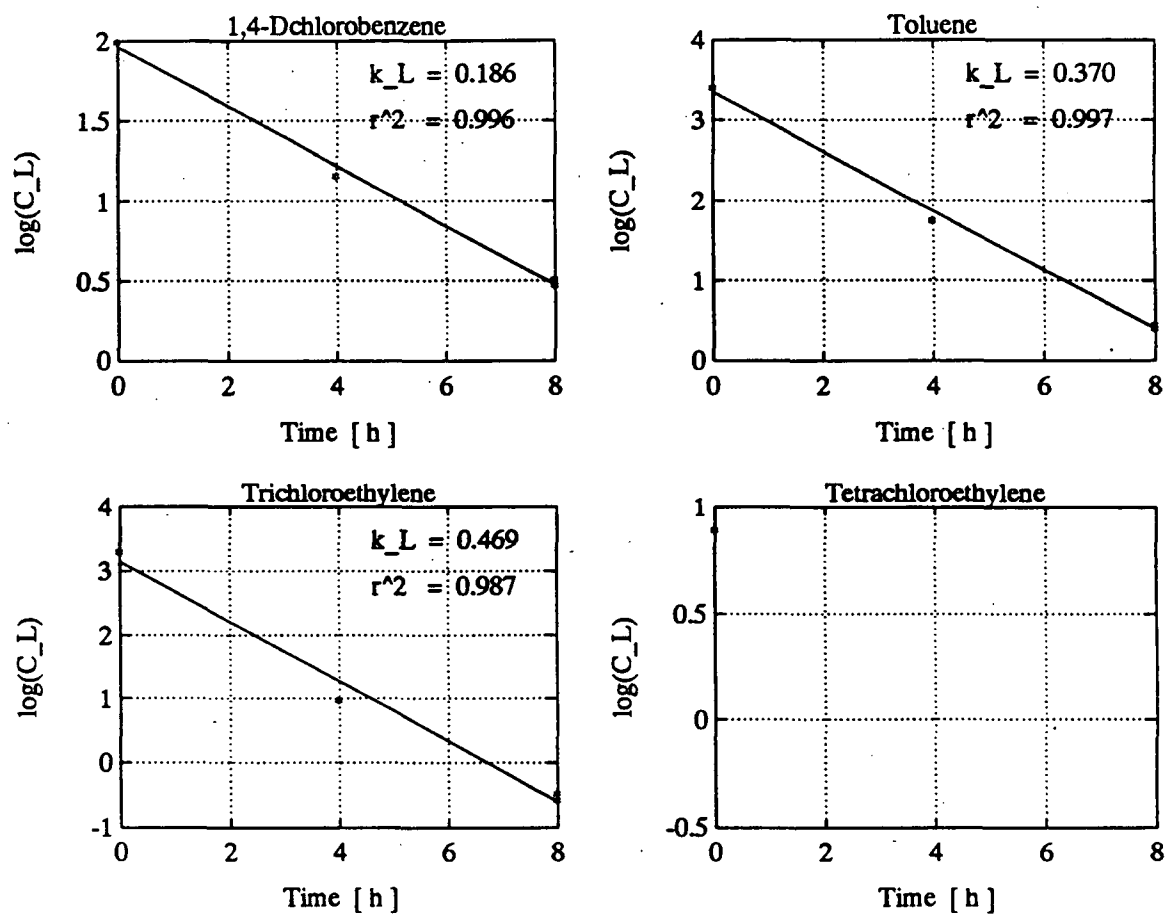


Figure II.4.7: Experiment 9 - Plot of $\ln C_L$ vs Time

The emission rate summary for the free ventilation experiments with a straight pipe drain connection is presented in Table II.4.15. The Table format is identical to Table II.4.11 discussed in Section II.4.3.2.

Methanol was not detected in the flux box effluent gas during any of the four experiments. Thus, the maximum E_G and $E_{G,rel}$ were calculated based upon the gas measurement method detection limit. There was not a consistent decline in the methanol wastewater concentration over the experiments and E_L could not be calculated.

For experiment 7 through 9 the average emission rates, calculated from the wastewater concentration, were the same order of magnitude as the emission rates calculated from the gas measurements. As discussed in Section II.4.3.2, this indicates that the two methods of measurement were comparable when emissions due to miscellaneous leaks were a small percentage of drain emissions.

For experiments 7 through 9, the relative emission rates of the VOCs, expressed as a percentage of the final wastewater concentration were significantly higher than those expressed as a percentage of the initial wastewater concentration because of the significant decline in wastewater concentration. The values expressed as a percentage of the initial and final wastewater concentrations represent the range of relative emissions. The actual relative emission rate should fall within this range. Based upon initial wastewater concentrations, the lowest relative emission rate was 0.45% for tetrachloroethylene and the highest was 5.64 for trichloroethylene. Based upon final wastewater concentrations, the lowest relative emission rate was 3.53% for 1,4-dichlorobenzene and 73.6% for trichloroethylene.

Table II.4.15: Emission Rate Summary - Free Ventilation With Straight Pipe Drain Connection

Compound	E_L (g/d)	E_{L1} (% of Initial liquid mass flowrate)	E_{L2} (% of final liquid mass flowrate)	E_a [T = 4 h] (g/day)	E_{a1} (% of Initial liquid mass flowrate)	E_{a2} (% of final liquid mass flowrate)	E_a [T = 8 h] (g/day)	E_{a1} (% of Initial liquid mass flowrate)	E_{a2} (% of final liquid mass flowrate)
Experiment Number 7 (no process flow)									
Methanol							< 1.3 E+2	< 5.8 E-2	< 6.1 E-2
1,4-Dichlorobenzene	2.6 E+1	1.0 E+0	2.4 E+0				8.3 E+1	3.0 E+0	7.7 E+0
Toluene	6.1 E+2	1.3 E+0	9.1 E+0				4.4 E+2	9.6 E-1	6.6 E+0
Trichloroethylene	1.2 E+3	1.4 E+0	1.2 E+1				1.3 E+3	1.6 E+0	1.4 E+1
Tetrachloroethylene	8.0 E+1	1.3 E+0	8.6 E+0				9.1 E+1	1.5 E+0	9.9 E+0
Experiment Number 8 (low process flow)									
Methanol							< 1.3 E+2	< 3.8 E-2	< 4.1 E-2
1,4-Dichlorobenzene	2.7 E+1	1.1 E+0	3.5 E+0	3.4 E+1	1.4 E+0	4.4 E+0			
Toluene	2.7 E+2	1.4 E+0	1.1 E+1	3.5 E+2	1.8 E+0	1.4 E+1			
Trichloroethylene	3.0 E+2	1.5 E+0	1.9 E+1	1.2 E+3	5.6 E+0	7.4 E+1			
Tetrachloroethylene	2.4 E+1	1.5 E+0	7.1 E+1	2.4 E+1	1.6 E+0	7.2 E+1			
Experiment Number 9 (high process flow)									
Methanol	< 1.6 E+2	< 5 E-2	< 5 E-2				< 1.6 E+2	< 5.0 E-2	< 5.0 E-2
1,4-Dichlorobenzene	2.1 E+1	1.0 E+0	4.6 E+0	1.7 E+1	7.8 E-1	3.5 E+0			
Toluene	1.1 E+2	1.2 E+0	2.5 E+1	4.5 E+1	5.2 E-1	1.0 E+1			
Trichloroethylene	9.9 E+1	1.3 E+0	5.8 E+1	3.8 E+1	4.8 E-1	2.2 E+1			
Tetrachloroethylene				3.1 E+0	4.5 E-1				

II.4.4 COMPARISON OF EMISSION RATES

Table II.4.16 summarizes the relative HAP emission rates observed during the free ventilation experiments. The relative emission rate of methanol was less than 0.1% under all operating conditions. With a P-trap drain connection and no process water flow into the drain, the relative emission rate of all VOCs was less than 0.1%. Without a P-trap, the emission rate of all VOCs was greater than 1% (with and without process water flow into the drain). This suggests that, for the highly ventilated system studied, significant mass transfer occurred in the sewer, but that the P-trap was effective at minimizing emissions by providing a vapor seal between the sewer air and the surrounding atmosphere.

With a P-trap drain connection, the presence of process flow into the drain substantially increased the emission rate of VOCs. The emissions were possibly caused by stripping as wind blows across the falling liquid between the end of the drain pipe and the mouth of the drain. Process flow into the drain did not substantially increase VOC emissions with a straight pipe connection.

Table II.4.16: Range and Median Emission Summary Calculated from Gas Measurements

Compound	$E_{G,rel,median}$ (%)	$E_{G,rel,median}$ (%)	$E_{G,rel,median}$ (%)
	$E_{G,rel,min} - E_{G,rel,max}$	$E_{G,rel,min} - E_{G,rel,max}$	$E_{G,rel,min} - E_{G,rel,max}$
P-trap Drain Experiments	Experiment 3 & 4 (no process flow)	Experiment 5 (low process flow)	Experiment 6 (high process flow)
Methanol	< 0.054 < 0.038 - < 0.069	< 0.072 < 0.068 - 0.075	< 0.047 < 0.044 - < 0.049
1,4-Dichlorobenzene	0.013 0.007 - 0.019	2.6 1.1 - 4.0	2.6 1.6 - 3.6
Toluene	0.014 0.007 - 0.021	2.4 0.5 - 4.3	4.1 1.1 - 7.0
Trichloroethylene	0.029 0.012 - 0.046	5.3 1.0 - 9.7	14.7 2.2 - 27.1
Tetrachloroethylene	0.037 0.009 - 0.064	7.5 0.7 - 14.2	27.8 1.9 - 53.7
Straight Pipe Drain Experiments	Experiment 7 (no process flow)	Experiment 8 (low process flow)	Experiment 9 (high process flow)
Methanol	< 0.060 < 0.058 - < 0.061	< 0.040 < 0.038 - < 0.041	< 0.052 < 0.050 - < 0.054
1,4-Dichlorobenzene	5.4 3.0 - 7.7	2.9 1.4 - 4.4	2.2 0.8 - 3.5
Toluene	3.8 1.0 - 6.6	8.0 1.8 - 14.1	5.4 0.5 - 10.3
Trichloroethylene	7.7 1.6 - 13.8	39.6 5.6 - 73.6	11.3 0.5 - 22.1
Tetrachloroethylene	5.7 1.5 - 9.9	36.6 1.6 - 71.6	0.5

II.5 MASS TRANSFER RATE SUMMARY

As presented in Section II.4.3.2, a first order rate of decline in wastewater concentration from a batch process can be expressed as:

$$\frac{dC_L}{dt} = -k_L C_L \quad (1)$$

where C_L is the wastewater concentration and k_L is the effective mass transfer coefficient for the system. This mass transfer coefficient lumps all transfer mechanisms and would change as operating conditions change. Integrating this equation from time 0 to time t provides the following equation:

$$C_L = C_{L0} \exp(-k_L t) \quad (2)$$

This can also be expressed in the following form:

$$\ln C_L = \ln C_{L0} - k_L t \quad (3)$$

The negative slope of a linear plot of $\ln C_L$ versus T represents the effective mass transfer coefficient based on the observed decline in wastewater concentration.

For experiments 3 through 9, mass transfer coefficients for each compound were calculated using the plots presented in Figures II-4.1 to II-4.7. These mass transfer coefficients were labelled $k_L(L)$ since they are based on the decline in wastewater HAP concentration during the experiment.

Mass transfer coefficients were also calculated using the gas phase VOC concentration measurements ($k_L(G)$). If losses from the system are solely due to air emissions at the drain connection, the following equation applies:

$$\frac{dC_L}{dt} = -Er \quad (4)$$

Therefore, $k_L(G)$ can be calculated using:

$$K_L = \frac{E_r}{C_L} \quad (5)$$

where:

E_r = Average Rate of VOC emissions from drain structure over length of experiment
 C_L = Average wastewater concentration during length of experiment.

Emission rate measurements were generally made once or twice during the experiment. Results were presented in Tables II-4.11 and II-4.15. To calculate the average emission rate over the length of the experiment, it was assumed that the emission rate declined over the length of the experiment at the same rate as the wastewater concentration declined.

A summary of the calculated $k_L(L)$ and $k_L(G)$ values is presented in Table II.5.1. The $k_L(L)$ values would include losses from all emission sources within the system and not only emissions occurring at the drain. If the emission rate at the drain structure was small, the other losses in the system would become significant, inflating the $k_L(L)$ value. However, if the emissions from miscellaneous leaks were a small percentage of drain emissions, there should be good agreement between $k_L(L)$ and $k_L(G)$. Thus, for experiments 3 and 4, for which measured emission rates were small, $k_L(L)$ values were significantly larger than $k_L(G)$. For these experiments, it is likely that $k_L(G)$ values better represent the mass transfer coefficient for drain emissions. Generally, there was acceptable agreement between $k_L(L)$ and $k_L(G)$ for experiments 5 through 9.

The impact of experimental conditions on the mass transfer coefficients ($k_L(G)$) for individual compounds is displayed in Figure II-5.1. Results for methanol are not presented, since it was not detected in any gas sample. For all compounds, mass transfer coefficients were less than $2.0 \times 10^{-3} \text{ h}^{-1}$ for the experiments in which the P-trap was in place with no process wastewater flow into the drain. With the p-trap, mass transfer coefficients increased with increasing process wastewater flowrate. This suggests that, with the P-trap in place, that emissions were induced by air blowing around the falling liquid stream and possibly by splashing within the trap. With a straight pipe connection (no p-trap), mass transfer coefficients were consistently greater than 0.1 h^{-1} under all experimental conditions and there was no consistent trend with regards to process wastewater flowrate into the drain.

Comparisons of the mass transfer coefficients for different compounds for each experiment are presented in Figure II-5.2. Methanol was not detected in any gas samples and maximum mass transfer coefficients, based on the analysis method detection limit, are presented. For experiments 3 and 4 (p-trap, no process water flow into the drain), the mass transfer coefficients for the VOCs increased with increasing volatility. In experiment 6 (p-trap, low process water flowrate into the drain) and 7 (p-trap, high process water flowrate into the drain) mass transfer coefficients generally increased with increasing compound volatility. For experiment 7 (straight pipe connection, no process wastewater flow into the drain) mass transfer coefficients for the VOCs were relatively constant, possibly indicating different mechanisms were inducing emissions. The emissions were likely induced by air being pulled

along the sewer and up the drain connection. For experiments 8 (p-trap, low process wastewater flow into the drain) and 9 (p-trap, high process wastewater flow into the drain), mass transfer coefficients generally increased with increasing volatility, as in experiments 3 through 6. This may suggest that emissions were induced by a combination of these mechanisms:

- air being pulled along the sewer and up the drain connection
- wind blowing across the falling liquid
- splashing within the p-trap

Table II.5.1 Summary of Mass Transfer Rates ($k_L(G)$)					
Compound	$k_L(L)$ (h ⁻¹)	$k_L(G)$ (h ⁻¹)	Compound	$k_L(L)$ (h ⁻¹)	$k_L(G)$ (h ⁻¹)
Experiment 3 P-trap, no presoco flow			Experiment 4, P-trap no presoco flow		
Methanol (H = 5.5 E-3 L gas/ L liq)		< 5.7 E-3	Methanol (H = 5.5 E-3 L gas/ L liq)		< 3.1 E-3
1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	1.7 E-2	1.5 E-3	1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	2.7 E-2	6.7 E-4
Toluene (H = 0.28 L gas/ L liq)	2.9 E-2	1.6 E-3	Toluene (H = 0.28 L gas/ L liq)	2.3 E-2	6.3 E-4
Trichloroethylene (H = 0.43 L gas/ L liq)	4.0 E-2	3.4 E-3	Trichloroethylene (H = 0.43 L gas/ L liq)	3.2 E-2	1.1 E-3
Tetrachloroethylene (H = 0.76 L gas/ L liq)	6.5 E-2	4.0 E-3	Tetrachloroethylene (H = 0.76 L gas/ L liq)	5.9 E-2	1.3 E-3
Experiment 5 P-trap, no presoco flow			Experiment 6, P-trap no presoco flow		
Methanol (H = 5.5 E-3 L gas/ L liq)		< 5.2 E-3	Methanol (H = 5.5 E-3 L gas/ L liq)		< 4.2 E-3
1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	8.5 E-2	1.3 E-1	1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	1.0 E-1	2.1 E-1
Toluene (H = 0.28 L gas/ L liq)	1.7 E-1	8.3 E-2	Toluene (H = 0.28 L gas/ L liq)	2.3 E-1	1.7 E-1
Trichloroethylene (H = 0.43 L gas/ L liq)	2.0 E-1	2.0 E-1	Trichloroethylene (H = 0.43 L gas/ L liq)	3.1 E-1	4.5 E-1
Tetrachloroethylene (H = 0.76 L gas/ L liq)	2.4 E-1	1.7 E-1	Tetrachloroethylene (H = 0.76 L gas/ L liq)	4.2 E-2	1.2 E-0
Experiment 7 P-trap, no presoco flow			Experiment 8, P-trap no presoco flow		
Methanol (H = 5.5 E-3 L gas/ L liq)		< 4.8 E-2	Methanol (H = 5.5 E-3 L gas/ L liq)		< 2.9 E-3
1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	1.2 E-1	3.4 E-1	1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	1.5 E-1	1.9 E-1
Toluene (H = 0.28 L gas/ L liq)	2.4 E-1	2.1 E-1	Toluene (H = 0.28 L gas/ L liq)	2.6 E-1	2.1 E-1
Trichloroethylene (H = 0.43 L gas/ L liq)	2.7 E-1	2.2 E-1	Trichloroethylene (H = 0.43 L gas/ L liq)	3.2 E-1	1.0 E+0
Tetrachloroethylene (H = 0.76 L gas/ L liq)	2.4 E-1	3.0 E-1	Tetrachloroethylene (H = 0.76 L gas/ L liq)	4.8 E-1	8.0 E-1
Experiment 9 P-trap, high presoco flow					
Methanol (H = 5.5 E-3 L gas/ L liq)		< 3.5 E-3			
1,4 Dichlorobenzene (H = 0.13 L gas/ L liq)	1.9 E-1	1.4 E-1			
Toluene (H = 0.28 L gas/ L liq)	3.7 E-1	3.0 E-1			
Trichloroethylene (H = 0.43 L gas/ L liq)	4.7 E-1	3.2 E-1			
Tetrachloroethylene (H = 0.76 L gas/ L liq)	--	--			

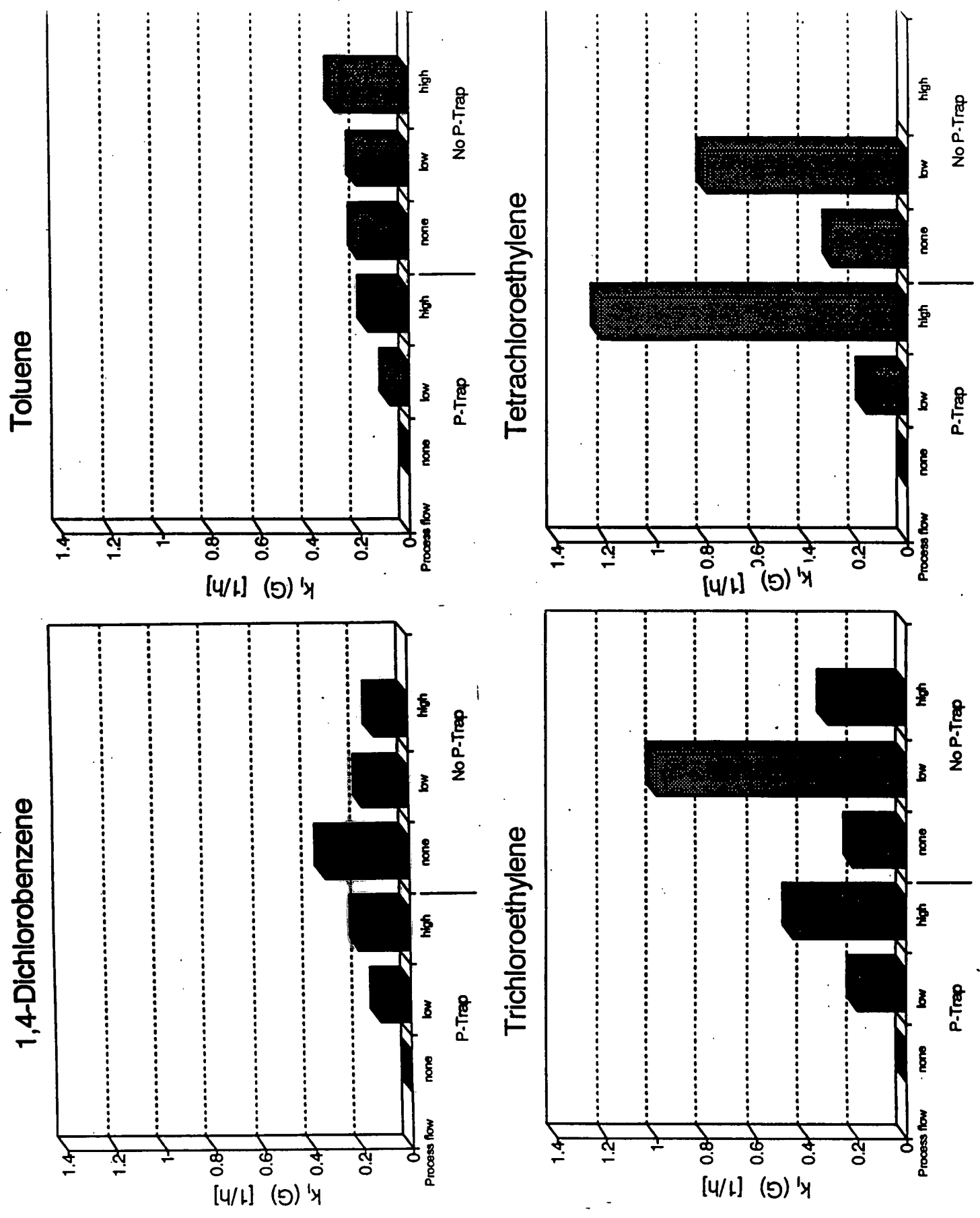
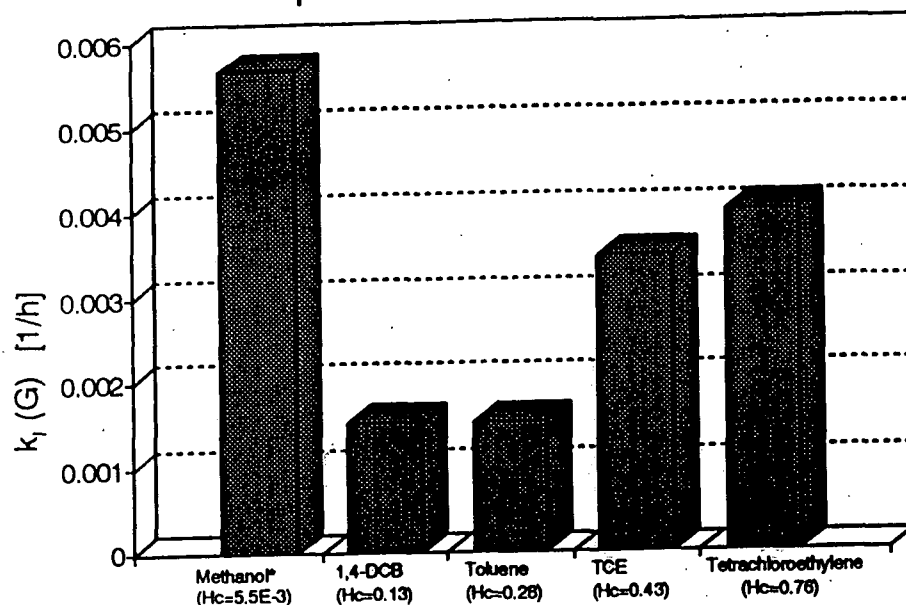


Figure II-5.1: Impact of Experimental Conditions on Mass Transfer Coefficients

Figure II-5.2: Impact Of Particular Compound On Mass Transfer Coefficients (Continued)

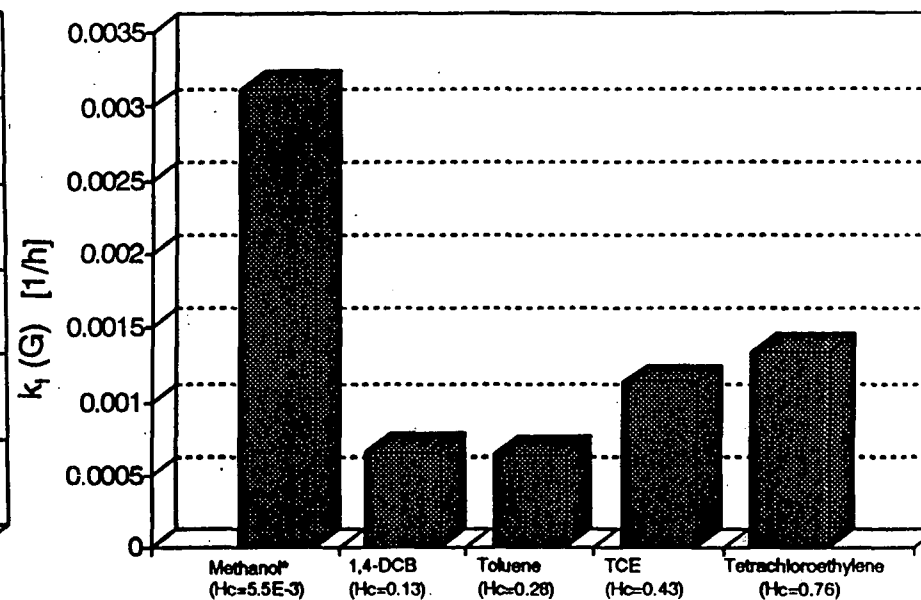
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Experiment 3



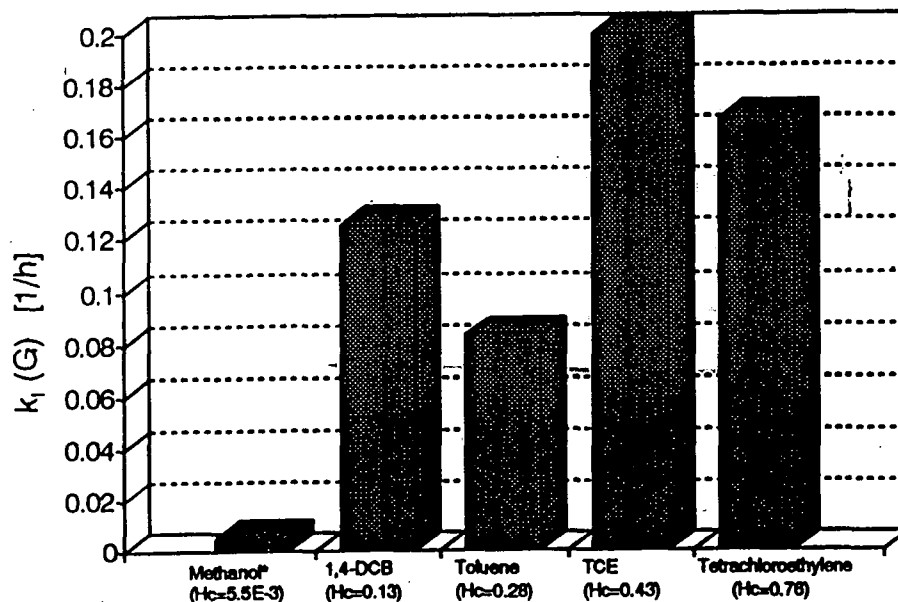
* max. value based on gas MDL

Experiment 4



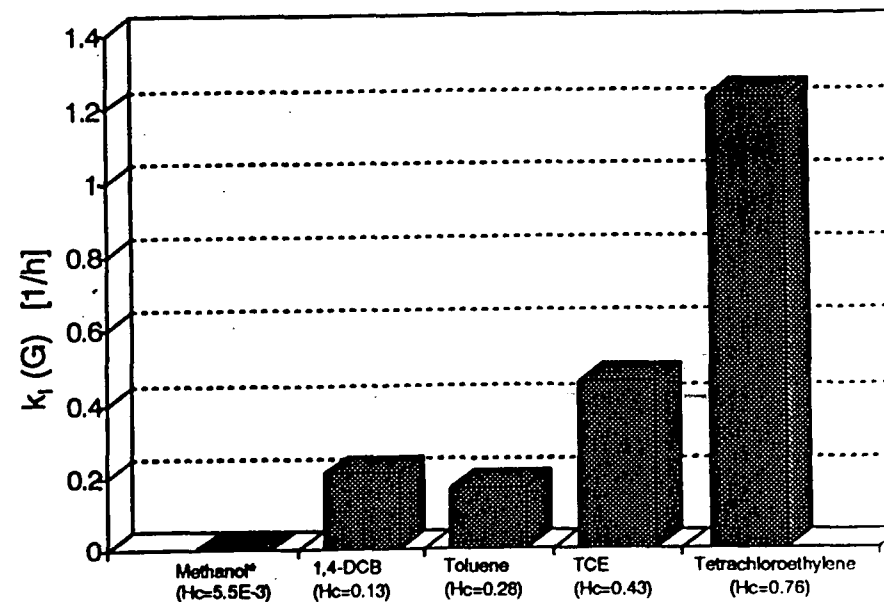
* max. value based on gas MDL

Experiment 5



* max. value based on gas MDL

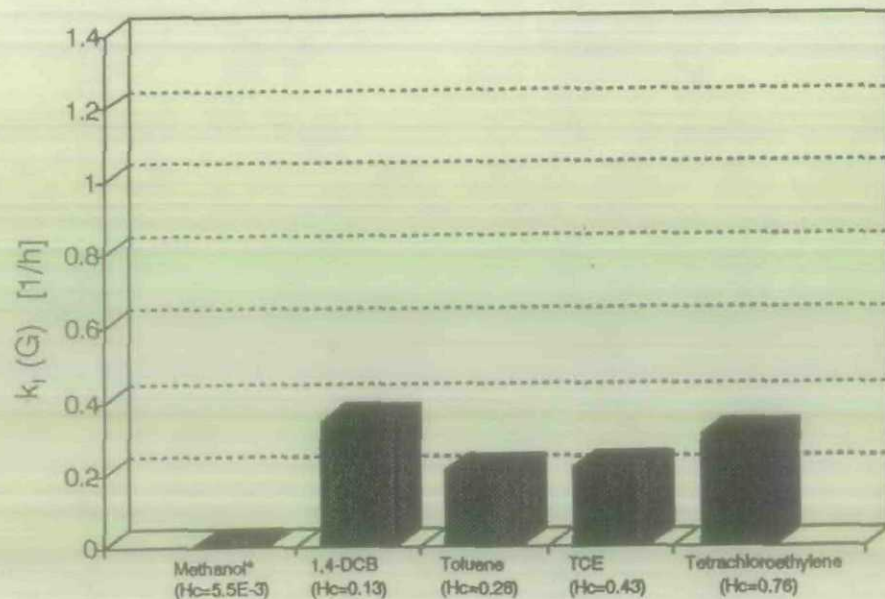
Experiment 6



* max. value based on gas MDL

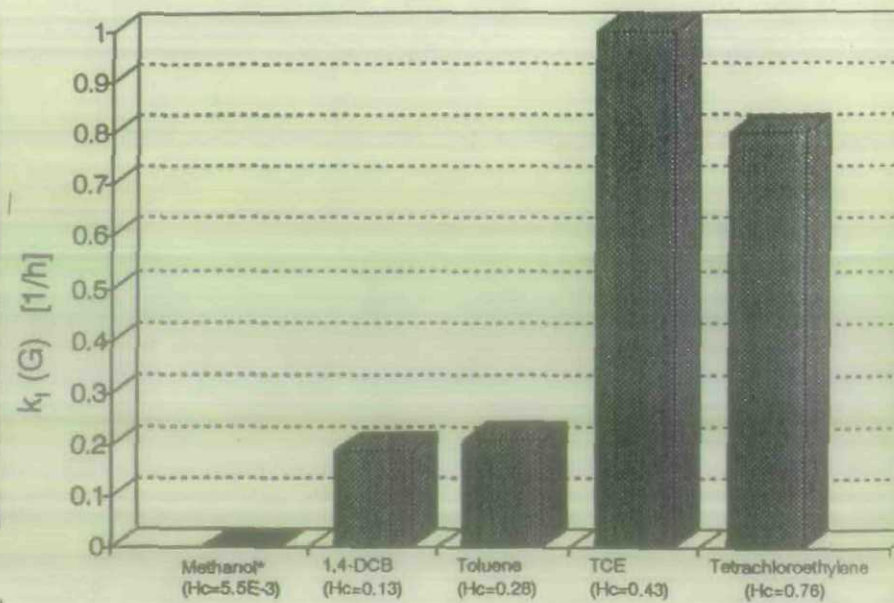
Figure II-5.2 Continued: Impact Of Particular Compound On Mass Transfer Coefficients

Experiment 7



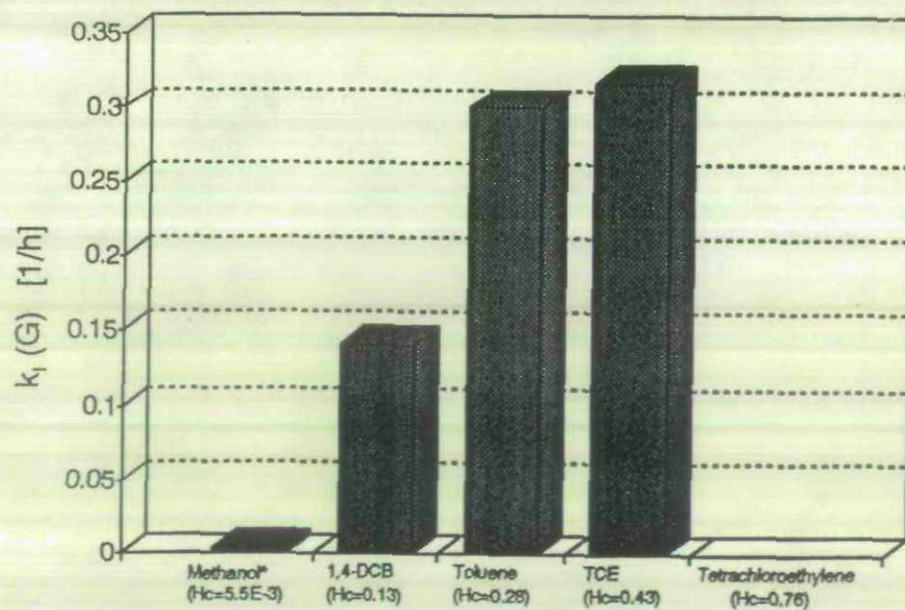
* max. value based on gas MDL

Experiment 8



* max. value based on gas MDL

Experiment 9



* max. value based on gas MDL

II.6 SUMMARY AND CONCLUSIONS

Nine experiments were conducted to measure HAP emissions from a pilot scale structure simulating a sewer and process drain connection. The sewer consisted of a 50 foot length of 4 inch diameter steel pipe. The drain consisted of a 4 inch diameter hub drain connected to the sewer by either a straight four inch pipe or a pipe with a p-trap. Experiments were conducted with no process wastewater flow into the drain and flowrates of 10% and 33% of the sewer flowrate. Tap water dosed with four VOCs and methanol was used as wastewater. The wastewater was continuously recycled during the experiments. A flux box was utilized to simulate a 7 km/h (4.2 MPH) wind blowing over the open drain.

Since wastewater was continually recycled throughout the experiments, the concentration of HAPs in the wastewater would decline if there were significant emissions (like a batch process). For each experiment, effective mass transfer coefficients (k_L) were calculated based on the observed decline in wastewater concentration. In addition, sampling of the flux box effluent air was used for direct measurement of the HAP emission rates. Effective mass transfer coefficients were also derived using the gas sampling results. Except for two experiments, there was good agreement between mass transfer coefficients measured using gas samples $k_L(G)$ and mass transfer coefficients calculated based on the decline in the wastewater concentration $k_L(L)$ during the experiment. For two experiments, in which the measured HAP emission rate was small (p-trap, no process water flow into drain), $k_L(L)$ values were significantly higher than $k_L(G)$ values. It is postulated that $k_L(G)$ better represented the actual mass transfer coefficient, when drain emission rates were small, because $k_L(L)$ was inflated by emissions from other sources (i.e. small leaks within the system).

The following conclusions are made as a result of this study:

- For the system studied, significant ventilation was observed within the sewer pipe when a straight pipe connection was used between the drain and the sewer. Airflow velocities greater than 1 m/s were observed in the sewer. The ventilation resulted from the combined effects of liquid drag and wind eduction.
- The p-trap provided an effective vapor seal, minimizing the air velocity within the sewer pipe to less than 0.2 m/s. The airflow likely resulted from swirling within the sewer headspace rather than a net movement of air.
- There was no significant decline in the wastewater concentration of methanol during any experiment, and methanol was not observed in any gas sample. Maximum mass transfer coefficient values (less than 1 E-2 h^{-1}) were calculated based on the analytical method detection limit for methanol in air.
- For all four VOCs, mass transfer coefficients were consistently less than 1 E-2 h^{-1} for the experiments in which the p-trap was in place with no process wastewater flow into the drain. Thus, the installation of p-traps could significantly reduce HAP emissions from process drains under some operating conditions. However, mass transfer coefficients increased significantly with process wastewater flow into the drain. It is

postulated that mass transfer was induced by air blowing across the falling liquid stream, above the drain mouth, and possibly by air swirling above the p-trap and splashing water. Mass transfer coefficients also increased with increasing compound volatility.

- With a straight pipe connection (no p-trap) and no process water flow into the drain, the mass transfer coefficients of the VOCs were consistently greater than 0.1 h^{-1} . It is postulated that emissions were induced by mass transfer between the water in the sewer and the overlying air drawn up the drain pipe. For the single experiment carried out, there was no observed effect of compound volatility on the mass transfer coefficients.
- Process water flowrate into the drain did not have a consistent effect on mass transfer coefficients when a straight drain pipe (no p-trap) was in place. However, mass transfer coefficients increased with increasing compound volatility. It is postulated that mass emissions were induced by three combined effects:
 - mass transfer between water in sewer and overlying air drawn up the drain pipe
 - stripping caused by wind blowing across the falling liquid above the drain mouth
 - mass transfer between swirling air above p-trap and splashing water